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(ZHURNAL ANALITICHESKOI KHIMII)

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

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SORPTION OF MOLYBDENUM AND RHENIUM FROM VARIOUS MEDIA ONTO THE ANION EXCHANGE RESIN EDE-10, AND THE CHROMATOGRAPHIC SEPARATION OF THESE ELEMENTS

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Rhenium, being one of the most scattered elements, does not form its own characteristic minerals and as a result of its physicochemical affinity with molybdenum, it is always associated with the latter in the natural state. Because of the similarity in their chemical properties, separation of rhenium and molybdenum is a difficult problem. All the same, differences in the stability of their various valency states do permit one to separate them from each other. Quite a few methods have already been published on the separation of molybdenum and rhenium.

One of the first methods suggested was distillation of rhenium as $ReCl_7$ or Re_2O_7 [1, 2]; this method was subsequently improved [3, 4] and used for mass analyses [5, 6]. The following precipitants have been used either alone or in various combinations for separating these elements: 8-hydroxyquinoline [7] and α-benzoinoxime [8] for molybdenum, and hydrogen sulfide [9, 10] and nitron acetate [11] for rhenium. Electrolytic methods of separating these elements have been developed on the basis of differences in the reduction potentials of these elements [12, 13]. Many papers have been devoted to extraction separation of molybdenum and rhenium; these include: extraction separation of the compound formed between molybdenum and xanthogenate with chloroform [14, 15], extraction of molybdenum cupferronate with organic solvents [16], extraction with chloroform of the compound formed between rhenium and tetraphenylarsonium chloride [17, 18]. In recent years chromatographic methods have started to find use for separating these elements. Rhenium was first separated from molybdenum on Amberlite 4B [19]. Molybdenum, in the form of potassium molybdate, was eluted with a buffer solution of boric acid – NaOH at a pH of 8.35. Rhenium was eluted with 5% NaOH. Molybdenum and rhenium were later separated by the same authors on a charcoal adsorbent – Norite [20]. This pair of elements has also been separated by other investigators using sulfo-coal K [21], or a combination involving the use of alumina and sulfo-coal K [22], and on Amberlite IRA-400 [23, 24]. In one of the latter cases, the molybdenum was eluted with 10% NaOH, and rhenium with 7 N HCl [23], while in the other, molybdenum was eluted with 1 N $K_2C_2O_4$, and rhenium with 1 M $HClO_4$ [24]. Very recently, Dowex-1 [25, 26] has been used for separating these elements.

In practically all the papers referred to above, in order to construct the elution curves, determination of the amount of molybdenum and rhenium in the filtrates has been carried out by normal analytical methods. Only in very few cases, for example as in [27], which dealt with the separation of rhenium and technetium, has use been made of the labelled atoms method whereby the separation process can be followed rapidly and accurately.

The work we have carried out on the chromatographic separation of molybdenum and rhenium was done with the aid of the Russian anion exchange resin EDE-10; this resin is characterized by high-exchange capacity, chemical stability, and mechanical stability, and can be used over a wide pH range. Studies were carried out under static conditions in HCl, HNO_3, H_2SO_4, and H_3PO_4, using the radioactive isotopes Re^{186} and Mo^{99}. The conditions which gave maximum differences in sorption of molybdenum and rhenium under static conditions were subsequently used for the separation of these elements in synthetic mixtures and natural objects on a column.

The behavior of rhenium and molybdenum on the anion exchanger EDE-10 under static conditions was

studied as follows. Anion exchange resin which had been freed from mineral impurities by treatment with hydrochloric acid was converted into the chloride, nitrate, sulfate, or phosphate by eluting the resin with a 1-2 M solution of the appropriate acid. After the resin had been washed free of excess reagent with water, it was dried in air, and 250 mg aliquots of it weighed into 100 ml flasks. To each aliquot was then added 25 ml of one of the test acids in known concentration; this was followed by addition of radiochemically pure Mo^{99} and Re^{186} as indicators; these were added in the form of Na_2MoO_4 and $NaReO_4$ respectively in an amount of 0.1-0.2 ml. When equilibrium had been reached – after six to seven hours – during continuous agitation, aliquots were taken from each flask and transferred to targets which were then measured for their γ-radiation with an AMM-4 γ-tube.

TABLE 1

Sorption of Mo and Re from Various Acid Media

Acid concentration	HCl		HNO_3		H_2SO_4		H_3PO_4		
	% sorption						concentration mole/liter	% sorption	
	Re	Mo	Re	Mo	Re	Mo		Re	Mo
pH 5	93.2								
pH 3		98	91.0	98.5	63.1	84.5			
pH 2		97.5	87.2	98.4	57.6	75.5			
0.001 g·eq/l									
0.01							0.01	95.0	98.0
0.1	69.5		68.6	92.5	24.8	46.0	0.1	76.0	97.4
0.5	17.4	90.8	38.7	54.6	20.1		0.5	50.0	88.8
1	15.9	25.2	28.3	35.1	16.6	30.0	1	23.7	83
2	16.6	17.6	17.7	10.8	17.0	20.2	2	4.2	72.8
3	17.0		10.5						
4	17.2	34.6	12.9	9.9	17.9	18.4	4	3.6	58.2
6	19.9	39.4	13.6	10.2	19.6	17.5	6	3.9	43.5
8	21.5	36.6	14.0	10.8	23	15.9	8	4.0	30.6
9		33.7		10.6					
10	19.1		15.6	12.9	23.2	21.0	10	8.5	26.4
12			14.6		24.4				

β-Radiation measurements were excluded on account of the absorptive effect of the media, particularly in the case of H_3PO_4 solutions. While in the case of HCl and HNO_3, the latter could be carefully removed by evaporation, when sulfuric acid was used we lost rhenium on evaporation because of the volatility of this element as Re_2O_7, and when H_3PO_4 was used, an absorptive layer was formed. Because of the insignificant amount of γ-radiation in the total spectrum of Re^{186}, we had to use a large amount of the latter in order to be able to carry out measurements based on γ-radiation.

Active preparations of Mo^{99} were measured using a lead filter 5.75 g/cm^2 thick [28]. The lead filter was used in order to exclude the effect of technetium radiation, since technetium is formed according to the reaction $Mo^{98}(n, \gamma)\,Mo^{99} \xrightarrow{\beta^-} Te^{99m}$, and is found in equilibrium with molybdenum.

Knowing the activity of the indicator introduced and the activity still remaining in solution, the percentage sorption of molybdenum and rhenium was calculated for each concentration of test acid.

It follows from the results given in Table 1 that appreciable sorption of molybdenum and rhenium is only observed in hydrochloric, nitric, and sulfuric acid media up to concentrations of these acids of up to 0.1-0.5 N, while sharp differences in sorption between these elements, which could be used for their separation, were not observed throughout the whole concentration range of these acids.

The sharp differences in sorption of molybdenum and rhenium observed when phosphoric acid media are used (Figure 1) are connected, presumably, with the fact that molybdenum forms an anionic type complex which is readily sorbed by the anion exchange resin. Maximum differences are observed at a concentration of 2M of phosphoric acid; sorption of molybdenum amounts to 72.8% at this concentration, whereas that for rhenium is only 4%. This difference permits the use of phosphoric acid for separating molybdenum and rhenium under dynamic conditions, the rhenium being eluted with 2M H_3PO_4, while molybdenum is eluted with 10% NaOH. All tests under dynamic conditions were carried out on a 12-cm-long column, 5 mm in diameter. The same resin with a particle size of 100-150 mesh, and in the phosphate form was used. Before the column was loaded with

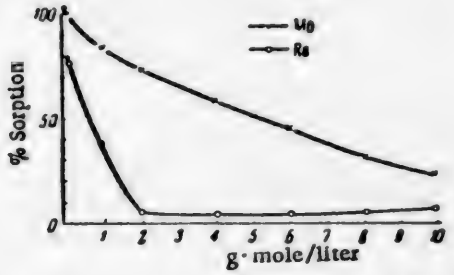

Fig. 1. Relation between sorption of Mo^{99} and Re^{186}, and H_3PO_4 concentration, on an EDE-10 anion exchange resin.

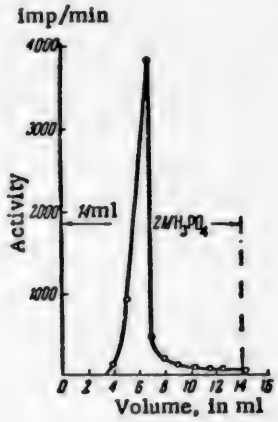

Fig. 2. Elution curve of Re^{186} with 2M H_3PO_4. Re^{186} added to the column had an activity of 5365 imp/min. Activity of the filtrate 5396 imp/min.

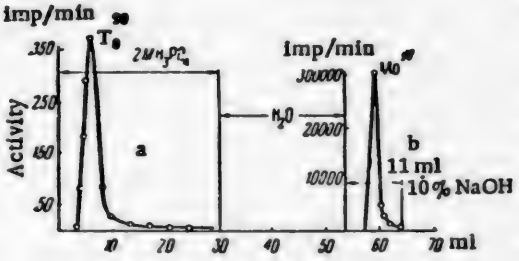

Fig. 3. Chromatographic separation of Tc^{99m} and Mo^{99}. Mo^{99} introduced onto the column, 49900 imp/min. Mo^{99} found in the filtrate, 49900 imp/min.

resin, the latter was washed with 2M H_3PO_4, an active preparation of Re^{186} in the form of sodium perrhenate was then transferred to the column; the amount introduced was 0.1-0.2 ml (5000-10,000 imp/min). Five to ten minutes after loading the column with rhenium, the latter was eluted with 2M H_3PO_4 at a rate of 0.07 ml/cm^2/min. Individual portions of the filtrate were collected on targets which were then measured for their γ-radiation. When 14 ml of eluate had been collected, no activity could be detected on the target; elution was then stopped at this point.

From the results of activity measurements of the targets, an elution curve was constructed (Figure 2). Complete elution of Re^{186} was determined by adding up the activities of the targets and comparing the total activity with a standard. From the results given in Table 2 it can be concluded that Re^{186} was eluted quantitatively.

In order to establish the reason for the fact that rhenium is eluted in the first portions of the eluate, the sign of the charge on the rhenium passing into the eluate was determined by means of electrophoresis. It was found that all the rhenium taken in the form of Re^{186} collected at the anode; no activity could be detected at the cathode. Consequently, rhenium, despite the fact that it was in the state of an anion, i.e., in the form favorable for sorption on the anion exchange resin, nevertheless passed into the eluate.

It is obvious that rhenium has been eluted from the sorbent by phosphoric acid. In order to check on this assumption, distribution curves of rhenium between the anion-exchanger and phosphoric acid solutions were taken under static conditions, the phosphoric acid concentration being kept constant, but the phosphate ion content being varied by addition of Na_3PO_4. Five flasks containing weighed amounts of resin were taken and Re^{186} added, 25 ml of 0.1M H_3PO_4 was then added to each, and Na_3PO_4 added in such amounts that the total concentration of PO_4^{3-} in the five flasks was 0.1, 0.5, 1, 2 and 4M respectively.

When equilibrium had been reached, aliquots were taken and γ-radiation measurements carried out. As the results given in Table 2 show, sorption of rhenium falls with increasing PO_4^{3-} concentration. Consequently, in acid media, rhenium is found in the form of an anion which passes into the filtrate as a result of the competitive action of acid anions.

The same column was used for studying the behavior of Mo^{99} under the conditions used for eluting Re^{186}, i.e., during elution of a resin containing Mo^{99} with 2M H_3PO_4.

Since Mo^{99} and Tc^{99m} are found in equilibrium with each other, we studied their combined behavior during elution with 2M H_3PO_4. In view of the close similarity between the chemical properties of rhenium and technetium, one would expect that the latter will behave like the former. For these tests, the active preparation of Mo^{99} in the form of sodium molybdate containing Tc^{99m} was placed on an anion exchange resin and the column eluted with 2M H_3PO_4 as described for rhenium. 2M H_3PO_4

TABLE 2

Relation Between Sorption of Re^{186} and PO_4^{3-} Ion Concentration

Concentration, (g·moles/liter)		Re^{186} introduced, in imp/min	Re^{186} found in the eluate, in imp/min	Re^{186} left on the resin, in imp/min	% Sorption
H_3PO_4	PO_4^{3-}				
0.1	0.1	1107	286	821	74.5
0.1	0.5	1107	719	396	36.0
0.1	1	1107	891	216	19.5
0.1	2	1107	986	121	11.0
0.1	4	1107	1085	22	2.0

TABLE 3

No. of test	Added				Found			
	Re		Mo		Re		Mo	
	in mg	(imp/min)	in mg	(imp/min)	in mg	(imp/min)	in mg	(imp/min)
1		1211	2			1252	2.10	
2		1211	2			1285	2.12	
3	2			5953	2.01			5897
4	2			5953	2.08			5905
5	4		4		4.1		4.18	
6	4		4		4.03		4.2	

was passed through the resin in an amount equal to twice the volume of acid necessary for complete elution of rhenium. The filtrate was analyzed for the presence of activity by means of γ-measurements. The measurements which are shown graphically on Figure 3a showed that toward the end of rhenium elution, there was observed some activity. On the basis of tests carried out under static conditions, this activity could not be ascribed to Mo^{99} since the latter should be efficiently sorbed under these conditions. Accordingly, the peak on Figure 3a belongs to Tc^{99m}. In order to make sure of this, the activity was identified on the basis of its half-life period and the maximum energy of its β-radiation. Results of these identification tests showed that the half-life period of 6.44 hours and the values of the energy, shown on Figure 4, are in good agreement with published results [29] for Tc^{99m}. No other activity could be observed on washing the column with 2M H_3PO_4.

The stable bond between molybdenum and the anion exchange resin in the given instance can be explained by the formation of an anion with a comparatively high charge. Apparently, molybdate ions and phosphoric acid react to form a heteropoly compound:

$$12Na_2MoO_4 + 9H_3PO_4 \rightarrow H_7[P(Mo_2O_7)_6] + 8Na_3PO_4 + 10H_2O.$$

It is precisely in this connection that molybdate and perrhenate differ from each other in their interaction with phosphoric acid.

After 30 ml of 2M H_3PO_4 had been passed through the column containing molybdate, the column was washed with water until the filtrate gave a neutral reaction. The molybdenum was then eluted off the column with 10% NaOH. This is made possible by the fact that the heteropoly acid, in which form Mo^{99} is held by the column, is destroyed by the alkali. The reaction can be depicted as follows:

$$H_7[P(Mo_2O_7)_6] + 27NaOH \rightarrow 12Na_2MoO_4 + Na_3PO_4 + 17H_2O.$$

During elution of the column with alkali, the eluate, in individual portions, was collected on targets and analyzed for the presence of Mo^{99} by measuring the γ-radiation. 11 ml of 10% NaOH was used for complete elution of Mo^{99}. The elution curve shown on Figure 3b was constructed on the basis of the experimental results

Fig. 4. Absorption of Tc^{99m} in aluminum: I) β-activity with an energy of 0.12 Mev; II) γ-activity.

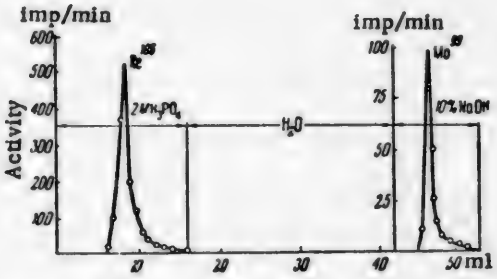

Fig. 5. Elution curves for indicator amounts of Re^{186} with 2M H_3PO_4 and a weighable amount of molybdenum (2 mg) with 10% NaOH.

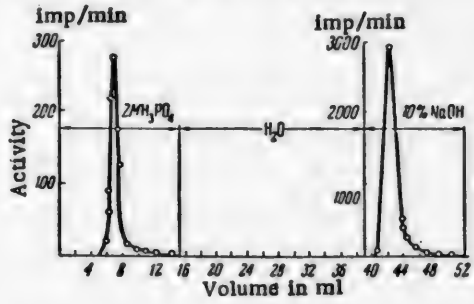

Fig. 6. Elution curves for weighable amounts (2 mg) of rhenium with 2M H_3PO_4 and for indicator amounts of Mo^{99} with 10% NaOH.

obtained. Completeness of elution of Mo^{99} was determined by adding up the activities of all the targets and comparing it with a standard. The results obtained indicated complete elution of Mo^{99}. Generalizing on the basis of all the results obtained, it can be stated that these elements are quantitatively eluted from the column by using 2M H_3PO_4 for eluting rhenium, and 10% NaOH for eluting the molybdenum.

The conditions established were used for separating synthetic mixtures of molybdenum and rhenium, and for isolating rhenium from natural objects. These elements were found in the following proportions in the synthetic mixtures used: 1) Re in indicator amounts, Mo in weighable amounts (2 mg); 2) Mo in indicator amounts, Re in weighable amounts (2 mg); 3) Re and Mo in weighable amounts (4 mg each). Elution of rhenium with 2M H_3PO_4 was controlled by Re^{186} activity and by means of the color reaction with $SnCl_2$ and KSCN, while for molybdenum the elution process was controlled on the basis of Mo^{99} activity and by the color reaction with potassium ethylxanthogenate. Elution curves for rhenium and molybdenum for cases 1 and 2 are shown on Figures 5 and 6.

The quantitative yield of indicator amounts of both elements was determined on the basis of the total activity in the appropriate portions of filtrate, while weighable amounts were determined on the basis of the reaction with nitron acetate in the case of rhenium [30, 31], and with lead acetate [32] for molybdenum (Table 3).

Of natural objects containing rhenium, we took molybdenite for testing.

Analysis of molybdenite for the purpose of isolating rhenium was carried out as follows. An aliquot of molybdenite contained in a conical flask was broken down with concentrated HNO_3 until all the molybdenum had been converted into molybdic acid. The white precipitate was dissolved in 10% NaOH in the same flask. The precipitated hydroxides of the heavy metals and undecomposed quartz were filtered off, and the filtrate acidified with phosphoric acid until the pH was 2. This solution was then passed through a column of EDE-10 20 cm long and 1 cm in diameter; the molybdenum was thereupon sorbed on the anion exchange resin while the rhenium was eluted by passage of 2M H_3PO_4 through the column at a rate of 2 ml/min. Completeness of removal of rhenium from the column was controlled on the basis of the disappearance of Re^{186} activity in the eluate, the Re^{186} having been added as an indicator, and by the disappearance of a color reaction with $SnCl_2$ and KSCN. An aliquot was then taken from the combined eluates and the rhenium content determined by the thiocyanate method [33, 34].

SUMMARY

1. Distribution of rhenium and molybdenum between the anion exchange resin EDE-10 and HCl, HNO_3, H_2SO_4, and H_3PO_4 solutions has been studied under static conditions using the radioactive isotopes Re^{186} and Mo^{99}.

2. A sharp difference was observed between the sorption of rhenium and molybdenum from phosphoric acid solutions; this can be explained by the fact that molybdenum, under these conditions, forms a complex anion which is readily sorbed by the active groups on the resin.

3. Synthetic mixtures of rhenium and molybdenum with varying proportions of the components have been separated under dynamic conditions; rhenium was eluted with 2M H_3PO_4 while molybdenum was eluted with 10% NaOH.

4. It has been shown that this technique can be used for isolating rhenium from molybdenites, and technetium from irradiated Mo samples.

LITERATURE CITED

[1] I. Noddack and W. Noddack, Z. ang. Chem. 44, 220 (1931).

[2] W. Geilman and F. Weibke, Z. anorg. Chem. 199, 120 (1931).

[3] E. Kronmann, Z. anal. Chem. 90, 31 (1932).

[4] I.P. Allmarin and B.N. Ivanov-Emin, J. Appl. Chem. 6, 1124 (1936).

[5] S.M. Basitova, Author's abstract* (1950).

[6] C. Hurd and F. Hiskey, Ind.Eng. Chem. 10, 624 (1938).

[7] O. Mikhailova, S. Pevzner and N. Arkhipova, Z. anal. Chem. 91, 25 (1933).

[8] A.D. Melaven and K.B. Whetsel, Anal. Chem. 20, 1209 (1948).

[9] J.H. Muller and W.A. La Lande, J. Am. Chem. Soc. 55, 2376 (1933).

[10] W. Geilman and G. Lange, Z. anal. Chem. 126, 321 (1944).

[11] W. Geilman and K. Brunger, Z. anorg. Chem. 199, 77 (1931).

[12] H. Holeman, Z. anorg. Chem. 202, 277 (1931).

[13] L.B. Rogers, J. Am. Chem. Soc. 71, 1507 (1949).

[14] V.I. Bibikova, Rare Metals 6, 24 (1933).

[15] E.E. Malouf and M.G. White, Anal. Chem. 23, (3), 497 (1951).

[16] N.H. Furman and W.B. Mason, Anal. Chem. 21, 1325 (1949).

[17] S. Tribalat, Anal. Chem. Appl. 3, 113 (1949).

[18] J.M. Beeston and J.R. Lewis, Anal. Chem. 25, N 4, 651 (1953).

[19] G.B. Alexander, J. Am. Chem. Soc. 71, 3043 (1949).

[20] G.B. Alexander, Ph.D. Thesis (University of Wisconsin, 1947).

[21] I.P. Kharlamov, Author's abstract of dissertation* (VIAM,** 1951).

[22] D.I. Riabchikov and A.I. Lazarev, Proc. Acad. Sci. USSR 92, 4, 777 (1954).

[23] S.A. Fischer and V.W. Meloche, Anal. Chem. 24, 1100 (1952).

[24] V.W. Meloche and A.F. Preuss, Anal. Chem. 26, 1911 (1954).

[25] E.H.J. Huffman, Inorg. Nucl. Chem. 3, 49 (1956).

*In Russian.

**All-Union Scientific Research Institute of Aviation Materials.

[26] K.A. Kraus and F. Nelson, Chemistry of Nuclear Fuel (Goskhimizdat, 1956).*

[27] R.W. Attebery and G.E. Boyd, J. Am. Chem. Soc. 72, 4805 (1950).

[28] Iu.B. Gerlit, Some Chemical Properties of Technetium* (Report read at the Geneva Conference, 1955).

[29] Radiochemistry,** Symposium edited by Spitsyn (Izd. MGU, 1952).

[30] R. Vouss and P. Bernays, Ind. Eng. Chem. Analyt. Ed. 12, 90 (1940).

[31] W. Geilman and A. Voigh, Z. anorg. Chem. 193, 311 (1930).

[32] A.M. Dymov, Technical Analysis of Metals** (Metallurgical Press, 1944).

[33] E.B. Sandell, Colorimetric Determination of Traces of Metals* (Goskhimizdat, 1949).

[34] W. Geilman and H. Bode, Z. anal. Chem. 128, 489 (1948).

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THE CHROMATOGRAPHIC METHOD IN QUALITATIVE ANALYSIS

IV. ANALYSIS OF CATIONS OF THE THIRD ANALYTICAL GROUP

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In the first article [1], material was presented which dealt with the establishment of adsorption series of cations and anions on the basis of their adsorbability on certain adsorbents, each group being taken separately. The second and third articles contained data obtained during a study of the development of chromatographic qualitative analysis of group IV and V cations on chromatographic alumina [2, 3].

The problem dealt with in the present article is development of a method for the chromatographic qualitative analysis of group III cations on chromatographic alumina.

The adsorption series of group III cations are arranged on adsorbents in the order indicated in Table 1.

TABLE 1

Adsorbent	Color of the adsorbent	Adsorption series
Chromatographic alumina	White	$Fe^{3+} = Cr^{3+} > Al^{3+} > Zn^{2+} > Co^{2+} = Ni^{2+} = Fe^{2+} > Mn^{2+}$
Permutite	White	$Fe^{3+} > Al^{3+} > Cr^{3+} = Zn^{2+} > Co^{2+} = Mn^{2+} = Fe^{2+} > Ni^{2+}$
Sulfunite	Light yellow	$Fe^{3+} > Al^{3+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Fe^{2+} = Ni^{2+} = Mn^{2+}$
Sulfo-coal	Black	$Fe^{3+} = Cr^{3+} = Mn^{2+} > Co^{2+} = Zn^{2+} = Ni^{2+}$

The cations Fe^{3+}, Co^{2+}, Ni^{2+}, and Cr^{3+} can be detected directly on the adsorbents chromatographic alumina and permutite. Only Fe^{3+} cations can be detected on sulfunite; the remaining cations form zones which are not clear cut with respect to color. Al^{3+}, Fe^{2+}, Mn^{2+}, and Zn^{2+} cannot be detected without additional development on the adsorbents.

Ni^{2+} cations can only be detected on chromatographic alumina when cobalt cations are absent in the solution, since, having equal adsorbabilities on the adsorbent indicated, the Ni^{2+} and Co^{2+} cations are adsorbed in the same zone. The same is true of Fe^{3+} and Cr^{3+}.

The limit of identification on alumina, without development, is 5.4 γ for Fe^{3+}, 35.0 γ for Co^{2+}, 35.0 γ for Ni^{2+}, and 30.0 γ for Cr^{3+}.

The cations were detected by the following technique. A test solution of the mixed cations of group III, mixed in equal volumes of solutions of equal concentration, was introduced by means of a pipet onto a chromatographic column 0.5 cm in diameter and 10 cm long packed with adsorbent. The chromatogram was washed with two to three drops of water, after which the developer was passed through the column. The adsorbed cations, located in different zones of the chromatogram, reacted with the reagent to give colored chemical compounds.

Experiments were carried out on columns packed with chromatographic alumina, permutite, sulfunite, and sulfo-coal.

TABLE 2

Adsorbent	Appearance of the developed chromatogram
Chromatographic alumina	A 0.3 N solution of group III cations was passed through the adsorbent. The chromatogram was washed with 5-6 drops of water. In the upper part of the column a brown zone terminating in a grey-blue band was formed which indicated the presence of Fe^{3+} and Cr^{3+} ions; below, there was formed a rose-colored zone of a mixture of Co^{2+}, Ni^{2+}, and Fe^{2+} cations. The chromatogram was developed with a saturated solution of Na_2HPO_4. The grey-blue Cr^{3+} zone became wider, while underneath it was found the violet zone of $Co_3(PO_4)_2$.
The same	A saturated solution of Na_2HPO_4 was passed through the column packed with adsorbent; this was followed by the test solution. A light yellow zone of $FePO_4$ was found at the top of the column; this was followed by a grey-blue $CrPO_4$ zone, and a violet $Co_3(PO_4)_2$ zone. Detection of Cr^{3+} cations by this technique gave a more clearly defined chromatogram with respect to the color of the zone than the technique described above.
Permutite	Test solution was passed through the column, and the chromatogram washed with water. Formation of colored zones could be observed visually: at the top of the column was found the orange zone of Fe^{3+} ions, below this was a narrow, blue zone, and below this, in turn, a green zone. The chromatogram was additionally developed with a saturated solution of Na_2HPO_4. From top to bottom the zones were arranged as follows: a brown Fe^{3+} zone, a blue Cr^{3+} zone, a violet Co^{2+} zone, and a greenish Ni^{2+} zone.
Sulfunite	Test solution was passed through the adsorbent, and the chromatogram developed with a saturated solution of Na_2HPO_4. Characteristically-colored zones could not be obtained, since, on passing the test solution through the column, there was formed a light yellow zone which is the characteristic color of the damp adsorbent, and this masked the color of the phosphates of the remaining cations.
Sulfo-coal	No colored zones were formed on developing the chromatogram with Na_2HPO_4 solution.

As the results of experiments numbers 1 and 2 of Table 2 show, Cr^{3+}, Fe^{3+}, and Co^{2+} can be detected when all three are present simultaneously on one column, by any of the techniques indicated.

Detection of Cr^{3+} ions in the presence of Fe^{3+} by means of a saturated solution of Na_2HPO_4 was much better on columns treated beforehand with the developer, i.e., by using a combined technique of precipitation and ion-exchange chromatography; precipitation chromatograms were therefore studied.

With this aim in mind, experiments were carried out on the formation of precipitation chromatograms of the third-group cations. The carrier used was alumina, while the precipitant was Na_2HPO_4. Mixtures of carrier and precipitant were prepared in different proportions: 99:1, 95:5, 90:10, 75:25, and 50:50. Experiments were carried out using the same technique as that employed for the formation of ion exchange chromatograms. The column was packed with a dry mixture of carrier and precipitant, ground to have a particle size of 0.25 mm; five drops of the test solution were introduced onto the column; colored zones were formed.

Experimental results showed that the optimum mixture of precipitant and carrier for obtaining precipitation chromatograms in the form of phosphate precipitates was a mixture of 50% Al_2O_3 and 50% Na_2HPO_4. The colors of the zones were brighter, while the sensitivity of detection was greater. Cr^{3+} ions could be detected in solution at a concentration of 0.065 N. Sodium hydrophosphate forms a bright yellow-colored precipitate of iron phosphate with Fe^{3+} ions. Experiments showed that on using a mixture of 50% Al_2O_3 + 50% Na_2HPO_4, even at a concentration of 0.25 g·equiv/liter of the iron salt, a brown Fe^{3+} was not formed, because all the Fe^{3+} ions were bound by the precipitant as the light yellow $FePO_4$; accordingly it was found possible to observe the grey-blue zone of $CrPO_4$ visually. Precipitation chromatograms have more clearly defined boundaries for the colored zones than ion exchange chromatograms. With decreasing concentration of the solution, the width of the developed zones decreased correspondingly.

Chromatograms of Group III Cations Developed With Ammonium Thiocyanate Solution

Five to six drops of a 0.3 N solution of a mixture of group III cations was passed through the adsorbent and, after washing with water, the chromatogram was developed with 2 N NH_4SCN solution. The results of these experiments are given in Table 3.

TABLE 3

Adsorbent	Appearance of the developed chromatogram (from top to bottom of the adsorbent column)
Chromatographic alumina	Blood-red zone of $Fe(SCN)_3$ gradually changing over into a brownish yellow zone (mixture of Fe^{3+} and Cr^{3+}). Violet-red zone of $Co(SCN)_2$. The $Co(SCN)_2$ zone, as a result of excess developer, gradually changed color to violet, characteristic of $(NH_4)_2[Co(CNS)_4]$.
Permutite	Blood-red zone of $Fe(SCN)_3$, yellow-brown zone with a green ring of Cr^{3+}; violet-rose zone of $Co(SCN)_2$.
Sulfunite	The zones in the chromatogram did not have clearly defined colors.
Sulfo-coal	No colored zones.

The results given in Table 3 show that the best chromatograms are those formed on alumina and permutite; these chromatograms permit detection of Fe^{3+}, Cr^{3+}, and Co^{2+} cations when they are all present together in solution.

Chromatograms of Group III Cations Developed With Alkali Solution

Detection of group III cations by means of alkali solution was carried out on various adsorbents: after passing a 0.3 N solution of group III cations through a column packed with adsorbent, the chromatogram was washed with water and developed with an alkali solution. The experimental results are given in Table 4. The best chromatograms for detection of Fe^{3+}, Co^{2+}, and Ni^{2+} are those obtained in experiments Nos. 1 and 2.

TABLE 4

Expt. No.	Adsorbent	Appearance of the developed chromatogram (from top to bottom of the adsorbent column)
1	Chromatographic alumina	A dark brown zone of $Fe(OH)_3$ was formed in the upper part of the column; below this was located a violet Co^{2+} zone; the zone of the Cr^{3+} ions was arranged in the form of a grey-blue band between Fe^{3+} and Co^{2+}. After a few hours a dark brown Mn^{2+} zone was found under the Co^{2+} zone; the manganese ions were in the form of Mn^{4+} ions which gradually acquired a black color. When chromatograms free from Mn^{2+} ions were developed with KOH solution, a brown zone was formed on top, while below this a violet zone of Co^{2+} ions was found. A black zone was not observed.
2	Permutite	Top – brown zone of $Fe(OH)_3$, below – violet Co^{2+} zone which gradually acquired a blue color. Below there was formed a green $Ni(OH)_2$ zone.
3	Sulfunite and sulfo-coal	No zones could be detected after development of the chromatogram with KOH.

Experiments were carried out on formation of chromatograms by the method of precipitation chromatography. The carrier used was anhydrous alumina, while the precipitant was sodium hydroxide; various mixtures were used with proportions of 9:1, 5:1, and 3:1. The test solutions were 0.25 N solutions containing from two to three cations of the third and fourth groups, which form colored zones with alkali.

The experimental results showed that precipitation chromatograms with brightly outlined zones were formed rapidly during filtration of the solution. The zones were arranged in order of the solubility products of the hy-

droxides. Fe^{3+}, Cu^{2+}, Co^{2+}, and Mn^{2} could be qualitatively detected in each others presence by precipitation chromatography in the form of the metal hydroxides.

Chromatograms of Group III Cations Developed With a Rubeanic Acid Solution

Five drops of a solution of a mixture of group III cations were passed through a column of adsorbent, the chromatogram was then washed with two drops of water, and developed with a 1% alcoholic solution of rubeanic acid.

The results of these experiments, which are given in Table 5, show that the use of rubeanic acid as a developer permits the detection of Ni^{2+} and Co^{2+} when these ions are simultaneously present in a solution of a mixture of group III cations.

TABLE 5

Composition of solution	Appearance of the developed chromatograms (from top to bottom of the adsorbent column)
Cobalt nitrate	Brown zone.
Nickel nitrate	Violet zone.
Mixture of nickel and cobalt salts	Violet-red zone.
Salts of Mn^{2+}, Fe^{2+}, Al^{3+}, and Zn^{2+}	All the cations form colorless zones.
A mixture of the salts of Fe^{3+}, Co^{2+} and Ni^{2+}	Dark brown zone of iron cations (III), violet-red zone of cobalt and nickel cations, bordered below by a narrow violet band – the nickel zone.
A mixture of the salts of Fe^{3+} and Ni^{2+}	Dark brown zone of iron (III) cations, violet zone of nickel cations.
A mixture of the salts of Fe^{3+} and Co^{2+}	Dark brown zone of iron (III) cations, light brown zone of cobalt cations.

The limit of identification of Ni^{2+} and Co^{2+} ions was found to be 0.13 γ, while the minimum concentration was 1:1,154,000.

Similar chromatograms were obtained on sulfunite, but the color of the zones was not so bright and the boundaries were not so clearly defined.

Chromatograms of Group III Cations Developed With Potassium Chromate Solution

A solution of the test cation was passed through the adsorbent and the chromatogram developed with 2 N K_2CrO_4.

The most characteristically colored zone was formed during the detection of manganese cations.

The experimental results (Table 6) show that the best chromatograms are formed when chromatographic alumina and permutite, treated beforehand with a solution of K_2CrO_4, are used as adsorbents.

Experiments were carried out on determination of group III cations by means of precipitation chromatography. Tests were carried out on columns consisting of anhydrous alumina as carrier and potassium chromate as precipitant; the ratios of the former to the latter chosen were 9:1, 3:1, 2:1, and 1:1. The best results were obtained with a mixture of 25% of K_2CrO_4 and 75% of anhydrous alumina.

Chromatograms of Group III Cations Developed With a Solution of Ammonium Tetrathiocyanatomercuroate

A solution containing Zn^{2+} and Co^{2+} cations was passed through the adsorbent, and the chromatogram developed with ammonium tetrathiocyanatomercuroate and nitric acid.

Table 7 shows that the best results are obtained for detection of Zn^{2+} ions when chromatographic alumina and permutite are used as adsorbents.

TABLE 6

Adsorbent	Appearance of the developed chromatogram
Chromatographic alumina	Test solution was passed through a column of adsorbent. The chromatogram was washed with K_2CrO_4 solution. On top of the column there was formed a bright brown zone of Fe^{3+} ions; this terminated in a green-brown ring of Cr^{3+} zones, while below this was a yellow zone. Beneath this zone was found a zone of Co^{2+}, Ni^{2+} and Fe^{2+} ions, and below this again a brown zone of Mn^{2+} ions. Formation of distinctly colored zones was only observed after a certain time, as the result of the conversion of Mn^{2+} to Mn^{4+}.
The same	The adsorbent was treated beforehand with a K_2CrO_4 solution; after 24 hours the test solution was passed through a column of this adsorbent. A black zone was formed in the lower part of the column. The chromatogram is better than in experiment No. 1.
Sulfunite	K_2CrO_4 solution was passed through a column of adsorbent; this was followed after 24 hours by the test solution. A dark brown zone was formed in the lower part of the chromatogram, manganese ions being probably present.
Sulfo-coal	No positive results were obtained.

TABLE 7

Expt. No.	Sequence in which the reagents are passed through the column of adsorbent	Appearance of the chromatograms on the adsorbents		
		chromatographic alumina	sulfunite	permutite
1	Saturated solution of Na_2HPO_4 + 4 drops of test solution + 2 drops of HNO_3 + ammonium tetrathiocyanatomercuroate.	A blue zone of Zn^{2+} ions is formed within 2-3 seconds.	A grey-blue zone whose boundaries were diffuse appeared after 5 minutes.	Blue Zn^{2+} zone appeared in 1-2 seconds.
2	4 drops of test solution + 2 N solution of HNO_3 + ammonium tetrathiocyanatomercuroate.	As in experiment No. 1.	Diffuse grey-blue.	The same
3	5-6 drops of test solution + 7-8 drops of ammonium tetrathiocyanatomercuroate + 2 drops of 2 N HNO_3.	Blue zone of Zn^{2+} ions formed in 2-3 seconds.	Blue Zn^{2+} zone after 2-3 minutes.	

When the techniques described in experiments Nos. 1 and 2 were used, on decreasing the concentration of Zn^{2+} and Co^{2+}, the zinc ions could no longer be detected at a concentration of 0.03 N, while when the technique described in experiment No. 3 was used, the Zn^{2+} ions could be detected at lower concentrations. The results show that Zn^{2+} can be detected in the presence of Co^{2+} ions at very low dilutions, namely at concentrations of the test solution of 0.00035 g·equiv/liter.

When no Co^{2+} ions are present in solution, it is necessary, before developing the chromatogram with $(NH_4)_2[Hg(SCN)_4]$, to pass one drop of a very dilute solution of a cobalt salt through the column. If Co^{2+} ions are present at a high concentration in solution – a fact which is readily apparent from the rose color of the solution – the solution should be diluted with water until the rose color of the solution is no longer visually observable; this diluted solution can then be tested for Zn^{2+} ions.

At high Co^{2+} concentrations, the latter may interfere with the detection of Zn^{2+} ions since cobalt forms a compound having a blue-violet color with $(NH_4)_2[Hg(SCN)_4]$, as a result of which Zn^{2+} may be mistakenly assumed to be present.

Co^{2+} ions can only be detected by means of $(NH_4)_2[Hg(SCN)_4]$ in the presence of HNO_3 at a concentration of 0.07 g·equiv/liter. At lower concentrations, Co^{2+} ions cannot be detected and the blue zone which appears on developing with $(NH_4)_2[Hg(SCN)_4]$ and HNO_3 belongs to zinc ions, which can be detected in solution at a concentration of 0.00035 g·equiv/liter in the presence of Co^{2+} in solution.

Chromatograms of Group III Cations Developed by Ammonium Hydroxide

A solution of a mixture of group III cations was passed through a column packed with chromatographic alumina, and after washing with water, the chromatogram was developed with 2 N NH_4OH. Experiments were carried out with solutions differing in composition from each other.

TABLE 8

Composition of solution	Adsorbent	Appearance of the developed chromatogram (from top to bottom of the adsorbent column)
Solution of a mixture of cobalt and nickel salts.	Chromatographic alumina.	Brown-violet zone of cobalt ammoniate, below which is a blue zone of nickel ammoniate.
Solution of a mixture of group III cations.	Chromatographic alumina and permutite.	Top – brown zone of ferric ions, followed by a brown-rose zone of cobalt ammoniate, and below this a blue zone of nickel ammoniate. The zone colors are brightest on permutite.
Solution of a mixture of group III cations but not containing Ni^{2+}.	Chromatographic alumina.	Top – brown zone of iron, followed by a brown zone of cobalt ammoniate.
Solution of a mixture of group III cations.	Sulfunite	The zone colors were not clearly defined; a blue Ni^{2+} was not observed.

The results given in Table 8 show that the best chromatograms, with respect to zone colors, are obtained on using chromatographic alumina and permutite.

Using chromatographic alumina, on which the adsorbability of Co^{2+} and Ni^{2+} ions is the same, it is possible to separate these elements as their complex ammoniates by using ammonia solution. Separation is based on the fact that cobalt ammoniate is adsorbed to a greater extent than nickel ammoniate; this corresponds to the adsorption series of the ammoniates established by Schwab $[Co(NH_3)_6]^{3+} > [Ni(NH_3)_6]^{2+}$.

Cr^{3+} ions can be detected at a concentration of 0.125 N, Ni^{2+} and Co^{2+} at 0.0125 N, and Fe^{3+} ions at 0.005 N.

On the basis of the results of the experiments described above a technique has been worked out for the chromatographic qualitative analysis of group III cations.

A Chromatographic Qualitative Method for the Analysis of Group III Cations (Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+})

In order to detect Fe^{3+} and Mn^{2+} ions, the test solution is passed through a column containing a 2-3 cm layer of chromatographic alumina. The appearance of a yellow-brown zone characteristic of $Fe(OH)_3$ indicates the presence of Fe^{3+} ions in solution. Mn^{2+} ions are detected in the filtrate issuing from the column. Since Mn^{2+} ions have such a low adsorbability, they are readily detected in the first drops of the filtrate by the reaction on filter paper with benzidene in ammoniacal solution.

Mn^{2+} can be detected directly on the adsorption column in the absence of Co^{2+} ions; for this purpose a column is prepared which contains a mixture of chromatographic alumina and potassium chromate with a particle size of 0.25 mm in the weight ratio of 3:1; the test solution is passed through this column. The formation of a dark zone in the lower part of the chromatogram, which gradually acquires a black color, indicates the presence of Mn^{2+} ions in the test solution. In addition, Mn^{2+} ions can be detected by passing the test solution through chromatographic alumina treated beforehand with three to four drops of concentrated alkali solution.

Formation of a dark brown zone which gradually turns black, and is located under the rose-colored zone of Co^{2+} ions indicates the presence of Mn^{2+} ions.

In order to detect Cr^{3+}, Co^{2+}, Ni^{2+} and Zn^{2+}, three to four drops of test solution are passed through a column of chromatographic alumina treated beforehand with five to six drops of a saturated solution of sodium hydrophosphate. In the upper part of the column is formed a white (with a hardly detectable yellow shade) zone of iron phosphate; below this is arranged the grey-green zone of chromium phosphate; this is followed by a rose-violet zone of cobalt phosphate.

In order to detect zinc ions a solution of $(NH_4)_2[Hg(SCN)_4]$ and two drops of 2N HNO_3 are passed through the column. A bright blue zone of Zn^{2+} ions is formed between the grey-green zone of the Cr^{3+} ions and the rose-violet zone of Cl^{2+} ions; the Zn^{2+} zone is in the form of a white precipitate of $Zn[Hg(SCN)_4]$ colored blue as the result of the presence of insignificant amounts of Co^{2+} ions. When no Co^{2+} ions are present, a fact which is readily established by the absence of a rose-violet colored zone in the primary chromatogram, it is necessary to pass a drop of a very dilute cobalt solution through the chromatogram before development with ammonium tetrathiocyanatomercuroate. When the test solution contains a large amount of Co^{2+} ions, which is evident from the rose color of the solution, then before the test it is essential that the solution be diluted with water until no rose color can be visually detected; at this point the solution can be tested further.

TABLE 9

Test solution	Developer	Limit of identification in γ, on 5 drops	Minimum concentration
$Fe(NO_3)_3$	Without developer	5.03	1:30000
$Co(NO_3)_2$	"	33.15	1:4000
$Cr(NO_3)_3$	"	9.62	1:15000
$Cr(NO_3)_3$	Sodium hydrophosphate	4.68	1:32000
$Co(NO_3)_2$	"	16.35	1:9200
$Fe(NO_3)_3$	Ammonium thiocyanate	10.33	1:14000
$Co(NO_3)_2$	Ammonium thiocyanate, concentrated solution	7.96	1:19000
$Mn(NO_3)_2$	Potassium chromate	3.71	1:40000
$Fe(NO_3)_3$	Sodium hydroxide	5.03	1:30000
$Co(NO_3)_2$	"	7.93	1:19000
$Mn(NO_3)_2$	"	0.91	1:160000
$Cr(NO_3)_3$	"	4.68	1:32000
$Fe(NO_3)_3$	Potassium ferrocyanide	2.51	1:60000
$FeSO_4$	Ferricyanide	0.21	1:710000
$Co(NO_3)_2$	Potassium ferrocyanide	1.98	1:76000
$Co(NO_3)_2$	Rubeanic acid	0.13	1:680000
$Ni(NO_3)_2$	"	0.13	1:680000
$ZnCl_2$	Ammonium tetrathiocyanatomercuroate + HNO_3	0.12	1:1250000
$Fe(NO_3)_3$	Concentrated ammonium hydroxide	2.51	1:60000
$Ni(NO_3)_2$	"	33.00	1:4500
$Co(NO_3)_2$	"	16.35	1:9200

In order to detect Ni^{2+} ions, four to five drops of test solution are passed through the column, and the chromatogram developed with ammonium hydroxide solution; the cobalt zone acquires a brown-violet color, while below this appears the blue zone of Ni^{2+} ions in the form of nickel ammoniate.

Ni^{2+} ions can be detected by development of the chromatogram with ammonia, after development of Zn^{2+} ions with ammonium tetrathiocyanatomercuroate in a second column. In the presence of sodium permutite, Ni^{2+}

can be detected by the formation of a green zone in the primary chromatogram, this zone being located below the rose-violet zone of Co^{2+}.

Ni^{2+} and Co^{2+} can also be detected by means of rubeanic acid. The reaction is very sensitive and permits detection of Ni^{2+} and Co^{2+} in amounts down to 0.13 γ during analysis with two drops of the test solution. In this case, two to three drops of test solution are passed through chromatographic alumina, and the chromatogram developed with rubeanic acid. When Ni^{2+} and Co^{2+} are present, there is formed a red-violet zone: when Co^{2+} ions are present while Ni^{2+} are absent, there is formed a brown zone of cobalt rubeanate in the form of an inner complex salt.

When Ni^{2+} is present and Co^{2+} absent, a blue-violet zone of nickel rubeanate is formed. Thus, the presence or absence of these two ions can be established on the basis of the color of the zone obtained.

Detection of Al^{3+} and Fe^{2+} is carried out directly on the test solution by means of spot reactions [4]. A complete analysis takes eight to ten minutes.

TABLE 10

Expt. No.	Method	Concentration, in g·equiv/liter	Amount of test solution taken for analysis, in ml	Time, in min, for carrying out an analysis	Experimental results
1	Macro method	0.0312	5	180	All cations were detected readily.
2		0.0156	5	160	Ni^{2+}, Co^{2+}, Al^{3+}, and Zn^{2+} detected very poorly.
3	Semi-micro method	0.0312	1	57	All cations were detected readily.
4		0.0156	1	45	Further dilution of the solution led to poor results.
5	Spot method	0.0312	1	20	All cations were detected readily.
6		0.0156	1	20	Further dilution of the solution led to poor results.
7	Chromatographic method	0.0312	0.5	8	All cations were detected readily.
8		0.0156	0.5	8	
9		0.0078	0.5	10	

Experiments were carried out in order to establish the sensitivity of reactions [5, 6] for group III cations with various reagents on chromatographic alumina. The results obtained are given in Table 9.

Experiments were also carried out on a comparative evaluation of various methods of detecting group III cations in solution.

Results of these experiments are given in Table 10. They demonstrate that the chromatographic method of analyzing group III cations has a number of advantages as compared with other methods. It only takes 8-10 minutes to carry out a chromatographic analysis of these cations, as against 20 minutes to 3 hours for the other methods. Chromatographic analysis can be carried out on a very small volume of test solution, and the amount of reagent used is 20-40 times less than that required for the macro and semi-micro methods.

The results of experiments Nos. 2, 4, 6, and 9 (Table 10) show that the chromatographic method is more sensitive than the others.

SUMMARY

1. It has been demonstrated that group III cations can be detected chromatographically when they are

present simultaneously in solution; they are detected on adsorbents – chromatographic alumina, permutite, and sulfunite – by means of various developers and precipitants.

A comparison of precipitation chromatograms with ion-exchange chromatograms showed that there was hardly any difference in the colors of the zones obtained. Nevertheless, precipitation chromatograms exhibit more clearly defined colored-zone boundaries.

2. A technique has been developed for the chromatographic qualitative analysis of group III cations, present together in solution, in which the adsorbent used is chromatographic alumina. Chromatographic analysis of group III cations can be carried out in the course of eight to ten minutes.

The limit of identification of each group III cation has been established for development on chromatographic alumina.

3. Various methods of detecting group III cations in solution have been compared. The chromatographic method is more rapid; it can be carried out with small amounts of reagents and minimum amount of test solution; it is also more sensitive than the other methods.

LITERATURE CITED

[1] K.M. Ol'shanova and K.V. Chmutov, J. Anal. Chem. 8, 211 (1953).•

[2] K.M. Ol'shanova and K.V. Chmutov, J. Anal. Chem. 9, 67 (1954).•

[3] K.M. Ol'shanova and K.V. Chmutov, J. Anal. Chem. 11, 1 (1956).•

[4] N.A. Tananaev, Spot Methods•• (GONTI, Goskhimizdat, 1939).

[5] V.N. Alekseev, Qualitative Analysis•• (Goskhimizdat, Moscow, 1943).

[6] I.P. Alimarin, Qualitative Semi-micro Analysis•• (Goskhimizdat, Moscow, 1952).

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THE APPLICATION OF PRECIPITATION CHROMATOGRAPHY ON PAPER FOR ANALYSIS OF INORGANIC CATIONS

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In an article published earlier [1] the possibility was demonstrated of using precipitation chromatography on paper as a spot variant in the qualitative analysis of inorganic cations. The present article contains results of investigations connected with an attempt to solve some problems in the theory of precipitation chromatography. Results are also given regarding the conditions for using this method for the analysis of inorganic cations (the values for the limits of identification in relative proportions).

Considerable attention has been given to a study of the effect of a series of factors on the development of the zones of the precipitates of individual cations. In carrying out these studies we pursued the aim of studying the possibilities of using precipitation chromatography as a method for determining the comparative solubility of precipitates, and also for establishing sorption series on the basis of the relative dimensions of the precipitation zones of individual cations. The main object was to establish the regularities between the width of the precipitate zone of various ions and the magnitude determining the zonal displacement and completeness of separation of the components of a test solution, which is one of the problems in the theory of precipitation chromatography.

1. The Relation Between the Dimensions of an Individual Cation Precipitation Zone and the Value of the Solubility Product of the Given Precipitate

In order to establish this relation, formation of the precipitates of individual cations was studied. 0.1 N solutions of the nitrates of the cations which one normally meets in the practice of qualitative analysis were used for the work. The volume of the drop of test solution was 0.025 ml. The concentration of the precipitant was calculated on the basis of the law of equivalence and the law of the conservation of matter.

In succession, the primary, washed, and developed chromatograms were prepared according to a technique described previously [2].

From a study of the formation of the precipitates of individual cations, it was established that:

1) The final zone dimensions of an individual cation precipitate were assumed by the washed chromatogram and not by the primary chromatogram.

2) On washing the primary chromatogram with solvent, the dimensions of the precipitation zone at first increased and then, after five to six washings, stabilized despite the further action of the solvent.

3) The final dimensions for the precipitation zones of individual cations, obtained on paper impregnated with the same precipitant, differed from each other and were found to exhibit a direct proportionality to the values of the solubility products of the precipitates formed.

Further experiments established a relation between these values, which could even be expressed in quantitative terms.

It was found, other conditions being equal, that the dimensions of the precipitation zones of two separate

cations on a washed chromatogram were inversely proportional to the indices of the solubility products of the given precipitates.

It should be pointed out that those values of the solubility products, the relative values of which determine the concentration of the test ions in the saturated solution above the precipitate, and on the ratios of which (according to the solubility product) the zonal distribution of the precipitates on the chromatogram depends, corresponded to this condition.

We should like to point out that the ratio of the dimensions of the precipitation zones of two individual cations on a washed chromatogram characterizes the relative mean rate of movement of the precipitates (the path traced by the precipitated ion during formation of a washed chromatogram).

Taking this fact into account, and designating the relative mean rate of movement of the precipitates by K_b, we can express the final relationship as follows

$$K_b = \frac{d_{M^+A^-}}{d_{K^+A^-}} = \frac{pL_{K^+A^-}}{pL_{M^+A^-}}, \qquad (1)$$

where $d_{M^+A^-}$ and $d_{K^+A^-}$ are the diameters of the precipitation zones corresponding to the least and most soluble compound respectively, and $pL_{M^+A^-}$ and $pL_{K^+A^-}$ are the indices of the solubility products of these compounds.

The establishment of a relation between the width of the precipitation zone of an individual cation and the solubility product of this compound permits one to:

1) assess the comparative solubility of precipitates formed on a chromatogram on the basis of the relative dimensions of the precipitation zones on a washed chromatogram;

2) establish the solubility series of precipitates by a chromatographic method, by making use of the direct relation between these values;

3) choose, deliberately, the precipitant and optimum conditions for the chromatographic separation of mixtures by means of a precipitation mechanism.

By studying the chromatograms of twin separations it was found possible to establish the numerical value of the coefficient K_b, by means of which it was possible to separate mixtures in the form of precipitates. It was found that a pair of inorganic cations can be separated by means of precipitation chromatography on paper, as long as the value of the coefficient K_b does not exceed 0.75. This corresponds to an interval in the values of the solubility products of the precipitates of the ions to be separated, of about three orders of units.

Further work showed that those ions which can be separated when present in pairs, can also be separated from more complicated mixtures. The zonal distribution of the components of a complex mixture on a precipitation chromatogram and the completeness of separation of this mixture, as tests have shown, are also determined by the value of the coefficient K_b.

It may be said that K_b, the coefficient of the mean relative rate of movement of the precipitate, has the same significance in the theory of precipitation chromatography as the R_f value has in partition chromatography.

2. The Chromatographic Solubility Series of Precipitates

Using the direct relation between the width of the precipitation zone of a single cation on a washed chromatogram and the value of the solubility product of the given precipitate, chromatographic solubility series of precipitates were established on paper which had been treated with: sodium arsenite, sodium hydrophosphate (the disodium salt), potassium iodide, sodium silicate, thiourea, potassium ferrocyanide, and potassium chromate.

The series obtained differed from one another according to the nature of the precipitant. These series, which are given below, are arranged in order of increasing solubility of the precipitates.

1. The series obtained on a paper impregnated with sodium arsenite

$$Hg^{2+}—Fe^{3+}—Cr^{3+}—Bi^{3+}—Al^{3+}—Cu^{2+}—Pb^{2+}—Ag^{+}—Cd^{2+}—Zn^{2+}—Co^{2+}—Ba^{2+}—Sr^{2+}.$$
$$\quad\;\; | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\;\; |$$
$$\quad Hg_2^{2+} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Ni^{2+}$$

2. The series obtained on a paper impregnated with sodium hydrophosphate (disodium salt)

$$Hg^{2+}-Fe^{3+}-Al^{3+}-Cr^{3+}-Bi^{3+}-Pb^{2+}-Cu^{2+}-Ag^{+}-Cd^{2+}-Mn^{2+}-Ni^{2+}-Sr^{2+}-Mg^{2+}.$$
$$\quad\quad\quad

As an example there are given below the final dimensions of the precipitation zone of silver chromate as a function of the concentrations used.

Concentration of the solution N	0.01	0.02	0.04	0.06	0.08	0.1
Width of the precipitation zone in mm	8.0	10.35	12.5	14.5	16.5	18.5

The results obtained confirm that the equation published earlier [3] can be satisfactorily applied for separation by precipitation chromatography on paper by an ascending method:

$$d = d_0 + Kc, \qquad (2)$$

where d is the width of the precipitation zone (in mm) at a given concentration of the original solution; d_0 is the zone width of the same precipitate for the lowest concentration of the test solution; K is a proportionality constant; and c is the concentration used.

The relation expressed by Formula (2) indicates the possibility of carrying out a quantitative determination of a single cation on the basis of the zone width of a precipitate of this cation on a washed chromatogram.

The proportionality coefficient K is determined graphically as the slope of a plotted curve.

4. The Effect of Other Factors on the Development of the Size of the Precipitation Zone of Separate Cations

Further work showed that the width of the precipitation zone of separate cations also depends on:

a) the volume (drop size) of test solution (direct relationship); b) precipitant concentration (inverse relationship; c) the nature of the precipitate formed (other conditions being equal, amorphous precipitates occupy wider zones than crystalline precipitates on washed chromatograms).

In calculating the effect of precipitant on the development of the precipitation zone of various ions, one must take into account the individuality of the cation and the anion which form the precipitate. This individuality is basically determined by the behavior of precipitate toward excess precipitant.

For precipitates which do not interact with excess precipitant, excess of the latter favors their complete separation on a narrower band. The zone boundaries of such precipitates are clearly defined.

In the case of precipitates which are capable of reacting with excess precipitant to form soluble complex compounds, excess precipitant leads either to diminution in zone size (as a result of its partial dissolution) or to complete dissolution of the precipitate formed.

Thus, a precipitate of mercuric iodide (the red modification) did not separate out at all on paper treated with 1% and 10% solutions of potassium iodide. On paper which had been impregnated with 4-5% precipitant solutions, while precipitates were formed, they dissolved appreciably during the process of preparing the washed chromatograms. The best-developed zone for this precipitate was obtained by using a 2% concentration of precipitant.

From what has been said, it follows that for complete deposition of precipitates which are capable of reacting with excess precipitant, the latter must be placed on the paper in amounts which are equivalent to the amounts of test cations.

5. The Effect of External Factors on the Formation of the Precipitation Zones of Individual Cations

Of the external factors which affect the development of the precipitation zones, the following were taken into account:

1) temperature changes; 2) the extent of physical adsorption; 3) the effect of other electrolytes; 4) interaction of test ion with solvent; 5) interaction of a given precipitate with other precipitates; and 6) pH changes in the medium.

It was found that temperature changes within the limits 10-30° do not lead to appreciable changes in the

TABLE 1

Reaction Sensitivity

Test cation	Limit of identification, in γ	Limiting dilution	Reagent used for developing the chromatogram
NH_4^+	10.5	1:2400	Sodium-p-nitrophenylazotate
K^+	40	1:625	Dipicrylamine
Mg^{2+}	30	1:835	Magneson I
Sr^{2+}	12	1:2100	Sodium rhodizonate
Ba^{2+}	5	1:5000	Sodium rhodizonate
Al^{3+}	5.5	1:4550	Alizarin
Cr^{3+}	2.4	1:10400	Benzidene
Fe^{3+}	1.0	1:25000	Potassium ferrocyanide
Mn^{2+}	0.35	1:71500	Benzidene
Zn^{2+}	0.3	1:88500	Dithizone
Ni^{2+}	60	1:420	Thiourea
Ni^{2+}	3.0	1:8350	Rubeanic acid
Co^{2+}	36	1:1700	Thiourea
Co^{2+}	0.75	1:33000	Rubeanic acid
Ag^+	25.0	1:1000	Potassium chromate
Hg_2^{2+}	20.0	1:1250	Thiourea
Hg_2^{2+}	12.5	1:2000	Potassium iodide
Pb^{2+}	14.0	1:1800	Sodium rhodizonate
Pb^{2+}	6.5	1:3850	Potassium iodide
Hg^{2+}	25.0	1:1000	Potassium iodide
Bi^{3+}	4.5	1:5560	Thiourea
Bi^{3+}	12.5	1:2000	Potassium iodide
Cu^{2+}	2.5	1:10000	Rubeanic acid
Cu^{2+}	2.5	1:10000	Dithizone
Cd^{2+}	1.25	1:20000	Cadion
Cd^{2+}	1.25	1:20000	Dithizone

development of the size of the precipitation zones of individual cations.

The part played by the paper in physical adsorption is completely insignificant. All the same, the effect of physical adsorption on the part of the other precipitate, in individual cases, has a considerable effect on establishment of the final dimensions of the precipitation zone of various cations. In such cases, the other precipitate, in fulfilling the role of a sorption column, holds the cation in the test solution by physical sorption forces during filtration of the solution through the layer of precipitant-sorbent.

As a consequence, the precipitation zone of the test cation will not develop as it should, because of incomplete precipitation of this cation in its layer.

Studies carried out with the object of establishing the effect of other electrolytes on the development of the size of the precipitation zones of individual cations, showed that this effect is insignificant.

The effect of the pH of the medium on precipitate formation was also of interest.

The experiments carried out along these lines led to the following conclusions.

Washing with dilute acids, of precipitates obtained on reaction paper and which are soluble under static conditions, did not, in most cases, lead to solution of the precipitates. Thus, an attempt to use the phosphate method of separating and identifying cations – which had been suggested by Petrashen' [4] as a test-tube method – for analyzing the same cations by the method of precipitation chromatography on paper, did not lead to the expected results. Precipitates which were soluble in acetic acid were not freed from precipitates which were only soluble in mineral acids.

This can be explained by the fact that during filtration of an acid solution through paper, a large fraction of the hydrogen ions is combined by adsorption

TABLE 2

Limiting Ratios

Test cation	NH_4^+	Mn^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	K^+	Sr^{2+}	Ba^{2+}	Pb^{2+}	Mg^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}	Ni^{2+}	Co^{2+}	Hg_2^{2+}	Bi^{3+}	Zn^{2+}	Cu^{2+}	Cd^{2+}	Ag^+	Hg_2^{2+}	Pb^{2+}	Hg^{2+}	Bi^{3+}
	Precipitant Na_2SiO_3					Precipitant Na_2HPO_4	Precipitant Na_3AsO_3			Precipitant $K_4[Fe(CN)_6]$			Precipitant NaCl	Precipitant			Thiourea				Precipitant K_2CrO_4	Precipitant KI			
	Developer																								
Accompanying cations	Sodium p-nitrophenylanthranilazotate	Benzidene	Rubeanic acid			Dipicrylamine	Sodium rhodizonate			Magneson I	Alizarin	$K_4[Fe(CN)_6]$	Benzidene	Thiourea			Dithizone				K_2CrO_4	KI			
NH_4^+	1	60	400	1700	25	0.5	25	40	50	6	225	1330	346	25	60	35	285	2150	100	250	25	100	10	25	20
Na^+	12	3640	400	1700	500	15	70	120	100	30	225	1330	346	25	60	65	285	6450	500	875	50	100	200	50	100
K^+	12	3640	400	1700	500	1	70	125	100	30	225	1330	346	25	45	65	285	4300	500	500	50	100	40	50	50
Mg^{2+}	60	1820	100	20	100	10	14	30	20	1	25	665	60	12,5	20	32	150	4300	500	500	25	50	100	25	50
Ca^{2+}	120	1820	400	300	250	15	15	25	50	30	220	1330	24	40	60	65	285	6400	500	750	50	100	200	50	50
Sr^{2+}	120	1820	400	1700	500	30	1	25	50	30	120	1330	24	40	60	65	285	4500	475	900	50	100	200	50	100
Ba^{2+}	40	1270	136	580	175	10	14	1	35	15	75	470	10	10	20	22	100	1050	175	175	10	35	70	17,5	35
Al^{3+}	24	16	200	330	100	15	14	20	25	5	1	665	60	10	40	32	155	1075	250	500	25	50	100	25	50
Cr^{3+}	60	10	20	1	25	30	52	50	50	5	200	1330	1	5	35	65	285	10	500	500	10	100	200	50	50
Fe^{3+}	120	70	400	10	25	30	30	25	10	15	25	1	70	2	35	12	285	80	500	25	10	100	2	10	100
Mn^{2+}	35	1	200	1	100	20	23	15	10	5	30	1330	12	40	100	32	285	115	100	10	1	100	200	50	100
Zn^{2+}	60	1820	80	20	100	15	12	15	10	5	220	1330	70	1	20	65	285	1	100	25	50	100	200	50	100
Ni^{2+}	60	110	1	10	10	30	25	15	10	15	30	665	10	5	50	65	280	12	100	25	50	100	200	50	100
Co^{2+}	60	10	12	1	10	30	15	15	10	5	30	665	23	40	1	65	280	10	100	25	5	100	200	50	100
Ag^+	120	12	22	45	50	30	34	50	50	30	225	1330	115	40	70	65	25	2200	100	500	1	10,8	10	1	10
Hg_2^{2+}	120	1820	400	30	10	30	70	15	50	30	225	1330	115	40	70	1	275	2150	100	500	2	1	2	1	10
Pb^{2+}	120	3640	400	330	500	30	70	60	1	30	110	1330	60	40	70	65	285	2150	500	875	50	100	1	50	50
Hg^{2+}	60	3640	400	1700	10	30	70	60	30	30	200	1330	115	40	70	35	280	2150	500	500	50	7.5	10	1	10
Bi^{3+}	94	1820	400	330	500	30	65	30	20	30	200	1330	60	25	70	65	1	1500	100	10	10	100	10	10	1
Cu^{2+}	60	900	10	1.2	1	30	25	15	10	30	220	130	70	25	60	65	10	2150	1	25	10	3.2	6	50	100
Cd^{2+}	120	1820	200	12	250	30	56	80	50	30	60	1330	115	25	60	65	56	12	500	1	50	100	50	50	100

forces of the paper, and this strongly limits their effect on the precipitates formed. As a result of this, the size of the precipitation zone of an individual cation on a chromatogram washed with an acid solution hardly differs at all from that of the same precipitate washed with distilled water. For this reason, the acidity of the test solution does not appear to interfere during chromatographic separation of inorganic cations by precipitation chromatography on paper.

6. The Sensitivity of Reactions Used in the Qualitative Analysis of Inorganic Cations by Precipitation Chromatography on Paper. Limiting Ratios

The procedures and techniques employed in the qualitative analysis of cations by means of precipitation chromatography have been described previously [5]. In order to determine the sensitivity of the qualitative reactions and the values of the limiting ratios, a series of 15 test tubes was prepared. In the first of them was placed a solution containing 100 mg/ml of the test element, while in the next test tube was placed a solution which was twice as dilute as that in the first test tube. This process was continued so that any one tube contained solution which was twice as dilute as that of its predecessor; in this way the concentration of each element varied from 100 mg/ml in the first tube to 0.0061 mg/ml in the 15th tube.

The sensitivity of any particular reaction was established by pipetting a drop of test solution with a micropipet – the volume of a drop being 0.025 ml – onto reagent paper, the drop being taken from the fifteenth tube to start with. The primary, washed, and developed chromatograms were prepared in turn. If no color developed, or if it was not clearly defined, then a drop of test solution from the next (stronger) test tube was taken, this procedure being repeated until a clear-cut result was obtained. Results of these tests are given in Table 1.

The values of the limiting ratios (Table 2) were determined by comparison with standard chromatograms, the latter being chromatograms of single cations obtained during determination of the reaction sensitivity.

7. Quantitative Determination of Ions by Precipitation Chromatography on Paper

The possibility of carrying out a quantitative determination of single cations on the basis of the width of the precipitation zone of the cation on a washed chromatogram has already been noted (Paragraph 3).

No success was obtained for quantitative determination of a particular ion in a complex mixture by this method. In such cases the principle of limiting dilution suggested by Shemiakin and co-workers [6-7] was used. The principle of the method of limiting dilution, which is applicable to quantitative analysis of inorganic cations by precipitation chromatography, can be stated as follows: the test solution, having been diluted to a known limit with respect to any one particular ion, ceases to give a color reaction with a developer on the reaction paper. Knowing the value of the limiting dilution C, the extent of dilution of the original solution e, and the weight of the aliquot of sample A, the percentage content (P) of the element in the test sample can be determined by means of the formula:

$$P = \frac{C \cdot e \cdot 100}{A} \qquad (3)$$

The experimental results obtained showed that quantitative determination of ions by this technique, while not being very accurate (the error, in relative percentages, varied from 0.45 to 18.9), is characterized by its speed and simplicity.

It would appear that the given method could be used as an express method in quantitative analysis for the control of production, and in scientific research when no great accuracy is required, or it can be used in preliminary work.

SUMMARY

1. A qualitative and quantitative relationship has been established between the width of the precipitation zone of a single cation on a washed chromatogram, and the solubility product of the precipitate, as well as a qualitative relationship with respect to a number of other factors.

2. Results have been obtained on the sensitivity of some qualitative reactions used for the analysis of inorganic cations by means of a spot test variant of precipitation chromatography on paper; limiting ratios have also been determined.

3. Sorption precipitation series on paper treated with certain precipitants have been established.

4. A method has been suggested for the quantitative determination of an individual cation, which is based on the width of the precipitation zone for the given cation on a washed chromatogram; a method has also been suggested for the quantitative analysis of complex mixtures of inorganic cations by a drop variant of precipitation chromatography on paper, in which the principle of limiting dilution is used.

LITERATURE CITED

[1] D.A. Viakhirev and F.N. Kulaev, Trans. Commission on Anal. Chem. VI (IX)* (Izd. AN SSSR, 1955), p. 527.

[2] D.A. Viakhirev and F.N. Kulaev, Trans. Commission on Anal. Chem. VI (XI)* (Izd. AN SSSR, 1955), p. 528.

[3] M. Milone, G. Cetini and F. Ricca, Annali di chimica 43, 652 (1953).

[4] V.I. Petrashen', Trans. Fifth Mendeleev Session* 1928, p. 43; Bull. Northern Caucasus Industrial Inst. 1 (15), 1934, p. 121.

[5] D.A. Viakhirev and F.N. Kulaev, Trans. Commission on Anal. Chem. VI (IX)* (Izd. AN SSSR, 1955), p. 530.

[6] F.M. Shemiakin and Z.S. Mitselovskii, Author's Thesis No. 87279* (February 15, 1950).

[7] F.M. Shemiakin, Research in Chromatography* (Izd. AN SSSR, 1952), p. 186.

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RESEARCH IN THE ANALYTICAL CHEMISTRY OF THALLIUM

PART 1. COMPLEXOMETRIC DETERMINATION OF THALLIUM

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A fairly large number of methods have been published for the quantitative determination of thallium [1, 2]. All the same, at present there are no really specific, rapid, and reliable methods for the determination of thallium in various industrial and natural objects.

Many methods are based on precipitation reactions of univalent thallium, in particular, with various sulfur-containing reagents (thionalide, mercaptobenzothiazole, sodium diethyldithiocarbamate, etc.). A number of methods have been developed which are based on the oxidation of univalent thallium to the trivalent state, and on the reduction of trivalent thallium to the univalent state. Meanwhile, formation of complex compounds of trivalent thallium has hardly been used at all in analytical chemistry. Experiments have shown that, despite current opinion, the number of such compounds is large, but they have hardly been studied at all. The first to draw attention to this fact was Feigl [3]. Even the reaction between trivalent thallium ions and disodium ethylenediaminetetracetate (Complexon III, Trilon B) has not been studied sufficiently, and, consequently, has not found practical application.

According to the work of Flaschka [4] Tl^{3+} ions form a stable complex compound with ethylenediaminetetracetic acid; the direct method which he developed for thallium determination is based on the addition of excess magnesium complexonate to a weakly acid solution of Tl^{3+}, with subsequent titration of the Mg^{2+} ions liberated in an ammoniacal medium in the presence of Eriochrome Black T. The method is complicated to carry out and is not specific. The same is true of the complexometric determination of Tl^{3+} described by Foley and Pottle [5]: this method consists of titrating excess ethylenediaminetetracetic acid with a standard solution of $Th(NO_3)_4$ in the presence of Alizarin S at a pH of 3.5; the lower pH limit at which the complex Tl^{3+} compound is stable has not been established. Complexometric determination of univalent thallium is of no practical importance in view of its nonspecificity; a compound of univalent thallium with ethylenediaminetetracetic acid is only formed at high pH values [6].

Since existing methods for the complexometric determination of Tl^{3+} do not satisfy practical requirements, we undertook a further study of the possibilities of a complexometric determination of this element. In this connection, therefore, we first of all established the lowest pH value at which the complex compound formed between trivalent thallium and ethylenediaminetetracetic acid is stable, and then studied the possibility of carrying out a direct complexometric titration of Tl^{3+} ions at low pH values and sought for a suitable chemical indicator. The result of our work was the development of a direct, fairly selective method for the complexometric titration of Tl^{3+} in some technical materials.

EXPERIMENTAL

1. In order to prepare a solution of thallic sulfate, an accurately weighed aliquot of thallous sulfate was dissolved in water, and sulfuric acid (1:1) added until the concentration was 1-2 moles/liter; the univalent thallium was then oxidized by means of ammonium persulfate, excess of which was destroyed by boiling. The solution obtained was diluted with water in a standard flask; its concentration was checked by means of the 8-hydroxyquinolate method [7]. 1 ml of the $Tl_2(SO_4)_3$ solution contained 1.74 mg Tl.

2. A solution of $Tl(NO_3)_3$ was prepared by dissolving thallic hydroxide in 2 N HNO_3; after dilution, the solution contained about 0.5 mole/liter of free HNO_3. The solution was standardized by addition of an excess of a standard arsenite solution and then back titrating excess of the latter with iodine solution in the presence of bicarbonate. To the $Tl(NO_3)_3$ solution containing about 20 mg of Tl, and which had been neutralized with $NaHCO_3$, was added 25 ml of 0.01331 N As_2O_3 which had also been neutralized beforehand to the phenolphthalein end point with sodium bicarbonate. The solution was heated for three to five minutes until the thallic hydroxide had dissolved. On cooling, excess trivalent arsenic was titrated with 0.009949 N iodine in the presence of starch. 1 ml of this solution contained 0.784 mg of thallium.

3. A $TlNO_3$ solution was prepared by dissolving metallic thallium in nitric acid. The solution was standardized by the classical chromate method (0.896 mg/ml Tl).

4. A solution of Tl_2SO_4 was prepared by dissolving the exact weight of this salt in water. 1 ml of the solution obtained contained 1.042 mg Tl.

5. The Complexon III solution was purified and prepared by Blaedel and Knight's method [8]; methanol was used instead of ethanol. A 0.01 M solution of Complexon III was prepared by dissolving the exact amount of the preparation dried in air to constant weight; a 0.001 M solution was prepared by dilution of the 0.01 M solution.

6. A 0.1% solution of 1-(2-pyridylazo)-2-naphthol in methanol was used as the indicator for Tl^{3+} ions.

7. Buffer solutions were prepared by mixing 1 M CH_3COOH + 1 M CH_3COONa. Clark and Labs buffer solutions (0.2 N KCl + 0.2 N HCl) with pH values of 1.0, 1.2, 1.6, 1.8, and 2.0 were also used, as well as similar buffer solutions which were prepared by mixing 0.2 N K_2SO_4 and 0.2 N H_2SO_4. 1 M $CH_2Cl \cdot COOH$ and 2 N NH_4OH were used in addition, for creating the necessary pH value in the solution to be titrated.

8. Amperometric titration with a rotating platinum microelectrode (l = 4.5 mm, d = 0.5 mm) was carried out on the usual setup. The reference electrode was a saturated calomel electrode.

DISCUSSION OF RESULTS

The lower pH limit at which the complex of trivalent thallium with ethylenediaminetetracetic acid is stable, as well as the possibility of carrying out a complexometric titration of thallium at a pH of 1.0-2.0, were established by the amperometric method using a rotating platinum micro-cathode; a dropping mercury cathode was not used because of anodic dissolving of the mercury at the reduction potential of the Tl^{3+} ion [9]. Tl^{3+}, on a platinum electrode, gives a clearly defined reduction current, starting at a potential of about +0.5 volt (Figure 1). Amperometric titration was found to be possible without applying an external emf. The equivalence point was established by the disappearance of the reduction current of Tl^{3+}. Titration was carried out without removal of dissolved atmospheric oxygen on 20-25 ml; to the solution (1-5 ml) of $Tl(NO_3)_3$ or $Tl_2(SO_4)_3$ was added NH_4OH until the pH was 1-2 according to universal indicator paper; this was followed by 15-20 ml of one of the buffer solutions mentioned above. Results of titrating Tl^{3+} in supporting electrolytes of chloride and sulfate buffer solutions showed that (Figure 2) the lowest pH value at which Tl^{3+} can be titrated in 0.2 N chloride solution is somewhat higher (pH 1.4-1.6) than in 0.2 N sulfate solution (pH 1.0-1.2). This can be explained, presumably, by formation of chloride complexes of trivalent thallium which approximate in stability to the complex of thallium with ethylenediaminetetracetic acid at pH 1.0-1.2. The strong adsorption of thallium on the strongly basic anion exchange resin Dowex 1 from hydrochloric acid solutions, and the difficulty of eluting thallium from the column [10], indicate the possibility of the formation of stable chloride complexes of trivalent thallium. Complete removal of thallium from a column is only possible by using a solution free from chloride ions (4 M $HClO_4$ or HNO_3).

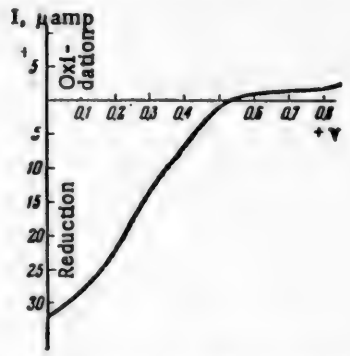

Fig. 1. Current-voltage curves for $4 \cdot 10^{-4}$ M $Tl_2(SO_4)_3$ in 1 N H_2SO_4.

Titration of Tl^{3+} with Complexon III at a pH of 1.0-2.0 in the presence of 0.2 M KBr is impossible be-

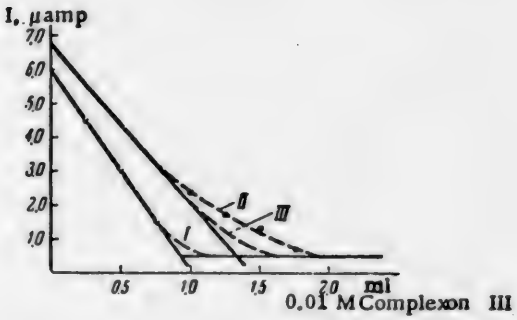

Fig. 2. Amperometric titration curves for $4 \cdot 10^{-4}$ M $Tl_2(SO_4)_3$ in 1 N H_2SO_4: I) in a supporting electrolyte of a sulfate buffer with a pH of 1.2; II) in a supporting electrolyte of a chloride buffer with a pH of 1.2; III) in a supporting electrolyte of a chloride buffer with a pH of 1.4.

cause of the higher stability of the bromide complexes of Tl^{3+} in the presence of excess Br^- ions. But on addition to a solution containing Tl^{3+} of potassium bromide in an amount corresponding to that theoretically necessary for formation of $TlBr_4^-$ ions, Br^- ions do not appreciably affect titration results, since in this case, the complex $TlBr_4^-$ dissociates to a considerable extent and is less stable than the complex with ethylenediaminetetracetic acid. Amperometric titration of Tl^{3+} with Complexon III in sulfate buffer solutions gives satisfactory results (Table 1).

Increases in the pH of the solution lead to a decrease in the reduction current of Tl^{3+} ions as a result of hydrolysis; this means an appreciable decrease in the sensitivity and accuracy of determination.

Since at present there is no suitable indicator for trivalent thallium ions, we studied an azo dye synthesized by A.E. Chichibabin [11] as an indicator; this azo dye has a pyridine ring as the first component 1-(2-pyridylazo)-2-naphthol. As Cheng and Bray [12] have shown, the azo dye gives intensely colored complexes with many cations (including Tl^+ at a pH of 10), and can be used for the complexometric determination of zinc and cadmium at pH 5-7, and of copper in an acetic acid solution. The azo dye is finding more and more applications as an indicator for the complexometric titration of a number of elements. We found that Tl^{3+} ions in nitric, sulfuric, and acetic acid solutions, at concentrations of 10^{-4} M and higher, form a red-violet complex with 1-(2-pyridylazo)-2-naphthol, starting at a pH of about 1. With decreasing Tl^{3+} concentration, the color change of the indicator from yellow to red-violet on addition of one drop of a solution of a Tl^{3+} salt, becomes clear cut at somewhat higher pH values, namely at 1.9-2.0. Chloride and bromide ions destroy the color of the complex by forming, presumably with Tl^{3+}, more stable complex compounds than the azo dye.

TABLE 1

Amperometric Determination of Thallium at pH 1.0-2.0

Thallium, in mg		Error		pH
taken	found	in mg	in %	
1.58	1.58	0	0	1.0
1.58	1.53	−0.05	−2.2	1.2
1.58	1.58	0	0	1.2
2.35	2.33	−0.02	−1.8	1.2
2.35	2.29	−0.06	−2.5	1.2
3.48	3.48	0	0	1.8
3.48	3.39	−0.09	−2.6	1.8
4.35	4.37	+0.02	+0.5	2.0
5.22	5.27	+0.05	+0.9	1.2

During titration of solutions of $Tl_2(SO_4)_3$ in the presence of 1-(2-pyridylazo)-2-naphthol with 0.01 M Complexon III, satisfactory results were obtained at a pH of 1.8-2.0 and higher (Table 2).

On the basis of the results obtained, the following indicator method has been developed for the complexometric determination of thallium.

To the solution containing Tl^{3+} ions is added 2 N NH_4OH, dropwise, until a bright yellow color develops [beginning of precipitation of $Tl(OH)_3$], an equal volume of 1 M $CH_2ClCOOH$ is then added, and the solution titrated with 0.01 M Complexon III in the presence of a few drops of indicator until the color changes from red-violet to yellow. 1 ml of 0.01 M Complexon III solution corresponds to 2.044 mg of Tl. During determin-

TABLE 2

Complexometric Titration of Trivalent Thallium in the Presence of 1-(2-Pyridylazo)-2-Naphthol

Thallium, in mg		Error		pH*	Thallium, in mg		Error		pH*
taken	found	in mg	in %		taken	found	in mg	in %	
0.69**	0.69	0	0	2.0—2.5	8.70	8.65	—0.05	—0.6	1.8
0.69**	0.68	—0.01	—1.4	2.0—2.5	8.70	8.71	+0.01	+0.1	2.0
1.38**	1.38	0	0	2.0—2.5	8.70	8.65	—0.05	—0.6	2.0
1.38**	1.37	—0.01	—0.6	2.0—2.5	8.70	8.71	+0.01	+0.1	2.1
3.48	3.45	—0.03	—0.9	1.6	8.70	8.71	+0.01	+0.1	2.1
3.48	3.46	—0.02	—0.6	4.0—4.5	8.70	8.65	—0.05	—0.6	2.6
3.48	3.50	+0.02	+0.02	4.0—4.5	8.70	8.71	+0.01	+0.1	2.8
4.35	4.28	—0.07	—1.6	1.3	8.70	8.70	0	0	3.6
4.35	4.39	+0.04	+0.9	3.5	8.70	8.70	0	0	3.8
6.96	6.90	—0.06	—0.9	1.5	8.70	8.76	+0.06	+0.7	4.0—4.5
8.70	8.59	0.11	1.3	1.2	8.70	8.65	—0 05	—0.6	4 0—4.5
8.70	8.60	—0.10	—0.9	1.4	26.11	26.06	—0.05	—0.3	4.0—4.5
8.70	8.59	—0.11	—1.2	1.7					

*Measured with a glass electrode. Although a glass electrode does not give accurate results at such pH values, nevertheless, the approximate results obtained completely characterize the possibilities of the method.

**Titration with 0.001 M Complexon III solution.

ation of Tl^+, it is oxidized first to Tl^{3+} by means of $(NH_4)_2S_2O_8$ at a H_2SO_4 concentration of 1 mole/liter. The method also gives good results for univalent thallium (Table 3).

Complexometric determination of Tl^{3+} with an indicator at a pH of 2 is possible in the presence of large amounts of Cd, Zn, and Pb (Table 4). In such cases, trivalent thallium in the form of a standard solution was added to a known volume of the solution of the metal salt and then titration carried out as usual.

TABLE 3

Complexometric Determination of Univalent Thallium (After its Oxidation to Tl^{3+}) in the Presence of 1-(2-Pyridylazo)-2-Naphthol

Thallium, in mg		Error	Thallium, in mg		Error
taken	found	in mg	taken	found	in mg
4.48	4.49	+0.01	5.21	5.18	−0.03
4.48	4.55	+0.07	5.21	5.22	+0.01
4.48	4.45	−0.02	1.04	0.95	−0.09
8.96	8.92	−0.04	1.04	1.03	−0.01
8.96	9.08	+0.12	1.04	1.05	+0.01
8.96	8.98	+0.02	0.73	0.74	+0.01
5.21	5.20	−0.01	0.54	0.47	−0.05

Cu^{2+}, Ni^{2+}, Fe^{3+}, and Bi^{3+} interfere with the visual titration of thallium when the indicator method is used since they form colored complexes with the azo dye at a pH of about 2 [12]; Cl^-, Br^-, and I^- interfere because they destroy the color of the complex formed between Tl^{3+} and 1-(2-pyridylazo)-2-naphthol, while colored MnO_4^-, Cr_2O_7, etc. ions also interfere. Consequently, it was of interest to get a more detailed idea of the effect of other ions during amperometric titration with Complexon III solution which should be more specific. Experiments showed that Cd^{2+}, Zn^{2+}, Pb^{2+}, and Ni^{2+} ions which do not give a reduction current at E = 0 volt, and do not form stable complex compounds with Complexon III at a pH of 1.0-2.0, do not interfere with the amperometric titration of Tl^{3+} (Table 5). Fe^{3+}, Bi^{3+}, Cu^{2+} which form complexes at pH 1.0-2.0 interfere with the amperometric determination of Tl^{3+} and should be removed beforehand. In the same way, ions of oxidizing agents which give reduction currents at E = 0 volt (MnO_4^-, $Cr_2O_7^{2-}$, $S_2O_8^{2-}$, etc.) interfere. Despite this, amperometric titration of Tl^{3+} possesses a number of advantages over visual titration, since it permits determina-

TABLE 4

Determination of Thallium in the Presence of Other Cations

Taken, in mg				Ratio	Found	Error
Tl	Cd	Zn	Pb	Tl: Me	Tl, in mg	in mg
8.70	86	–	–	1:10	8.67	−0.03
3.48	86	–	–	1:25	3.45	−0.03
3.48	258	–	–	1:70	3.50	+0.02
1.74	435	–	–	1:250	1.75	+0.01
1.74	4[illegible]	–	–	1:250	1.75	+0.01
3.48	234[illegible]	–	–	1:675	3.40	−0.08
3.48	2340	–	–	1:675	3.60	+0.12
3.48	2340	–	–	1:675	3.50	+0.02
3.48	–	227	–	1:60	3.40	−0.08
3.48	–	227	–	1:60	3.50	+0.02
1.74	–	454	–	1:250	1.79	+0.05
1.74	–	454	–	1:250	1.75	+0.01
1.57	–	681	–	1:400	1.56	−0.01
1.57	–	908	–	1:600	1.61	+0.04
1.57	–	1135	–	1:700	1.69	+0.12
6.96	–	–	1075	1:150	6.90	−0.06
6.96	–	–	1075	1:150	6.90	−0.06
3.48	–	–	1075	1:300	3.54	+0.06
3.48	–	–	2150	1:600	3.68	+0.20
3.48	–	–	2150	1:600	3.60	+0.12

TABLE 5

Amperometric Titration of Tl^{3+} in the Presence of Cd, Zn, Pb, and Ni

Added, in mg				Thallium, in mg		Error, in mg
Cd	Zn	Pb	Ni	taken	found	
258	100	100	50	2.35	2.37	+0.02
258	200	250	25	1.57	1.53	−0.04
344	200	250	100	2.35	2.35	0

tion in the presence of Cl^- ions at pH 1.4-2.0 and, furthermore, permits determinations to be carried out in turbid and colored solutions.

Determination of thallium in briquet cadmium. An aliquot of cadmium (1.0-1.5 g) is dissolved on heating in 10 ml of 2 N H_2SO_4 and 1-2 ml of concentrated HNO_3. The solution is heated on a sand bath to remove nitrogen oxides, about 0.1 g of $(NH_4)_2S_2O_8$ is then added (if a raspberry color appears because of the presence of MnO_4^-, 5 ml of 5% HCl is added; the MnO_2 formed does not cause any further trouble). The solution is next heated to remove excess $(NH_4)_2S_2O_8$ and neutralized with 2 N NH_4OH to a pH of about 2.0 using universal indicator paper; it is finally titrated amperometrically with 0.01 M Complexon III.

Determination of thallium in slag. An aliquot of test material is dissolved in 10-20 ml of 0.5 N HNO_3 and the univalent thallium oxidized by means of $(NH_4)_2S_2O_8$; the trivalent thallium is then titrated amperometrically with 0.01 M Complexon III solution at a pH of about 2.

In both cases, in order to check on the correctness of the results obtained (Table 6), a known amount of trivalent thallium was added to the solution after titration with Complexon III, and titration continued. In this way it was shown that the method gives satisfactory results for the determination of thallium in the materials indicated.

TABLE 6

Determination of Thallium in Technical Products

Test sample	Weight, in g	Tl found, in %	Tl added, in %	Amount of Tl that should be present, in %	Amount actually found, in %	Error, in %
Briquet cadmium (containing 0.15% Tl according to factory analysis)	1.2635	0.19	0.31	0.50	0.54	+0.04
	1.1686	0.16	0.46	0.62	0.59	−0.03
	1.3402	0.18	0.18	0.36	0.36	0
	1.3402	0.18	0.30	0.48	0.47	−0.01
Slag	0.1503	1.30	1.56	2.86	2.88	+0.02
	0.2181	1.24	–	–	–	–
	0.2204	1.31	1.07	2.38	2.46	+0.08
	0.2067	1.17	1.51	2.68	2.66	−0.02

SUMMARY

1. It has been shown that it is possible to carry out an amperometric titration of trivalent thallium with Complexon III at pH ≥ 1.2 (in the absence of large amounts of Cl^- and Br^- ions), and at pH ≥ 1.4 (in the presence of appreciable amounts of Cl^-).

2. 1-(2-Pyridylazo)-2-naphthol serves as an indicator for Tl^{3+} and permits visual titration of Tl^{3+} with Complexon III at a pH of about 2 and higher.

3. Large amounts of Zn, Cd, and Pb do not interfere with the complexometric determination of thallium. The method is suitable for the analysis of technical materials.

LITERATURE CITED

[1] R. Fresenius and G. Jander, Handbuch der analytischen Chemie T. III, B. III, Verlag Chemie, Berlin, 1942.

[2] J.R.A. Anderson, Anal. Chem. 25, 109 (1953).

[3] R. Feigl, Nature 161, 436 (1948).

[4] H. Flaschka, Microchemie 40, 42 (1952).

[5] W.T. Foley and R.F. Pottie, Anal. Chem. 28, 1101 (1956).

[6] R. Pribil and Z. Zabransky, Collection Czechoslov. Chem. Communs 16, 554 (1951).

[7] F. Feigl and L. Baumfeld, Anal. Chim. Acta 3, 83 (1949).

[8] W.I. Blaedel and M.T. Knight, Anal. Chem. 26, 741 (1954).

[9] O.A. Songina and A.P. Voiloshnikova, Factory Labs. 22, 19 (1956).

[10] K.A. Kraus, F. Nelson and G.W. Smith, J. Phys. Chem. 58, 11 (1954).

[11] A.E. Chichibabin and M.D. Riazantsev, J. Russ. Chem. Soc. 47, 1582 (1915).

[12] K.L. Cheng and K.H. Bray, Anal. Chem. 27, 782 (1955).

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THE USE OF COMPLEXONS IN POLAROGRAPHY

PART 2. THE BEHAVIOR OF MOLYBDENUM ON THE DROPPING MERCURY ELECTRODE IN A SUPPORTING ELECTROLYTE OF COMPLEXONS*

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The polarographic behavior of molybdate ions in acid solutions has been studied several times [1-6]. All the same, the mechanisms of the electrode reactions which occur cannot be regarded as established because of the complexity of the chemistry of sexivalent molybdenum; this is particularly true, since hitherto there has been no agreement between the data given for the nature of the molybdenum ions at various pH values. Many workers consider that the molybdate ion (MoO_4^{2-}) only exists at a pH of 7 and higher; on increasing the acidity, the ions $Mo_3O_{11}^{4-}$, $Mo_6O_{21}^{6-}$, $Mo_{12}O_{41}^{10-}$, and $Mo_{24}O_{78}^{12-}$ are formed, while at a pH of about 1, molybdenum may even be found in solution as the cation [7].

Some work has been carried out on the behavior of molybdate ions on a dropping mercury electrode in the presence of complexing agents. For example, Uhl [8] reduced molybdate in dilute solutions of nitric acid containing lactic and oxalic acids, and obtained two waves. The half-wave potential of the first was $E_{1/2} = -0.35$ volt, while that of the second was $E_{1/2} = -0.5$ volt (relative to the saturated calomel electrode). Nevertheless, as Johnson and Robinson [5] have pointed out, in the presence of nitrate ions there is obtained a catalytic wave for NO_3^- at the potential corresponding to the reduction of Mo^V to Mo^{III}, a fact which Uhl did not take into account; he was thus led to wrong conclusions. Good waves have been obtained for phosphomolybdic and silicomolybdic acids [9]. Recently, for analytical purposes, we suggested a method for determining micro amounts of molybdenum on the basis of the catalytic wave obtained in $HClO_4$ solutions [10]. Complexon III permits polarographic determination of molybdenum in the presence of tungsten and a number of other cations [11].

Results are given in the present article of a study of the behavior of the complexes formed between molybdenum and Complexon I (nitrilotriacetic acid) and Complexon III (disodium ethylenediaminetetracetate) respectively, on a dropping mercury electrode, as well as of a study of the behavior of the complexes formed between molybdenum and some new complexons; the effect of various factors were studied (pH, complexon concentration, height of the mercury column, etc.).

The work was carried out on a recording polarograph with a galvanometer whose sensitivity was $3.33 \cdot 10^{-9}$ μamp/mm/m. The capillary characteristics were $m = 1.98\ mg \cdot sec^{-1}$; $t = 4.2$ sec; $t^{1/6} = 2.00\ mg^{1/6} \cdot sec^{-1/2}$. The electrolyzer was provided with a sleeve through which water from a thermostat operating at 25 ± 0.1° was circulated. The anode was a saturated calomel electrode which was connected to the electrolyzer through an agar-agar bridge, prepared from a semi-saturated solution of potassium chloride. The values quoted throughout for the potentials are relative to the saturated calomel electrode. The pH was measured by means of an AP-4 tube potentiometer.

Ammonium molybdate solution was prepared by dissolving MoO_3 in a small excess of ammonia, the solution was then boiled until the odor of ammonia was no longer observable, and was finally diluted with water to the requisite volume. The molybdenum content was determined gravimetrically as lead molybdate.

*Part 1, see J. Anal. Chem. 8, 333 (1953) (see C.B. translation).

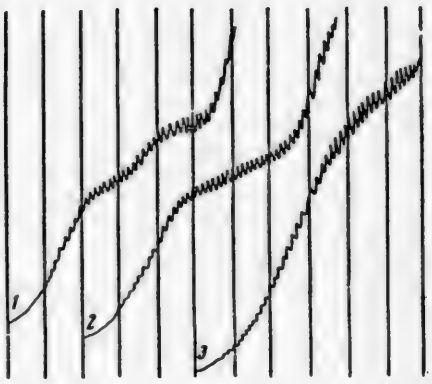

Fig. 1. Polarograms for ammonium molybdate ($1.04 \cdot 10^{-3}$ M) in a supporting electrolyte of acetic acid: 1) 5 M CH_3COOH; 2) 10 M CH_3COOH; 3) 15 M CH_3COOH.

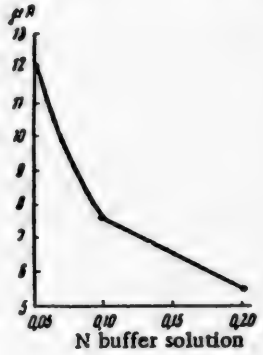

Fig. 2. Relation between the value of the diffusion current for molybdate ions and the concentration of the buffer solution of 0.1 N acetic acid and 0.1 N ammonium acetate, pH 4.6.

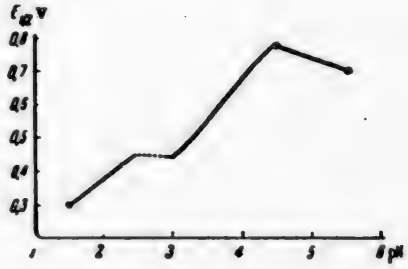

Fig. 3. Relation between the value of $E_{1/2}$ for molybdenum in the presence of Complexon I and pH: Mo concentration = $= 1.04 \cdot 10^{-3}$ M; Complexon I concentration = 0.05 N (in 0.1 N acetate buffer).

Solutions of lead, cadmium, and tungsten salts, as well as solutions of the other necessary materials, were prepared by dissolving the chemically pure preparations or analytical grade recrystallized salts.

The buffer solution with a pH of 4.6 consisted of equal volumes of 0.1 N acetic acid and 0.1 N ammonium acetate.

All the complexons were dissolved in the buffer solution. Complexons I and III were dissolved after recrystallization from a mixture of methanol and acetone (2:1).

On Figure 1 are shown the polarograms for molybdate ($1.04 \cdot 10^{-3}$ M) in 5, 10, and 15 M acetic acid. In 5 M acetic acid, molybdate gives two waves with $E_{1/2} = -0.27$ volt, and $E_{1/2} = -0.73$ volt. On increasing the acetic acid concentration, only one extended wave with a half-wave potential displaced to more negative values is obtained. In the buffer solution of 0.1 N acetic acid and 0.1 N ammonium acetate, with a pH of 4.6, the half-wave potential of molybdate is equal to -0.66 volt, and does not change with the changes in concentration of the buffer solution in the limits of 0.05-0.2 M. The value of the diffusion current decreases with increasing concentration of the buffer solution (Figure 2).

Complexon I. Molybdenum, in the presence of Complexon I gives a clearly-defined reduction wave in acid solutions; its half-wave potential depends on the pH. On Figure 3 is shown the relationship between $E_{1/2}$ and pH in a 0.1 N solution of acetate buffer and 0.05 M Complexon I.

As is evident from Figure 3, on increasing the pH from 1.5 to 4.5, the half-wave potential for molybdate shifts to more negative values. In the range pH 2.5-3, the wave breaks up into three waves and, on increasing the pH further, one wave is again obtained, the half-wave potential of which increases on the negative side; it reaches a maximum at 4.5 and then starts to shift gradually toward positive potentials. In alkaline solutions (pH 8-10) the wave disappears, indicating thereby the instability of the complex in alkaline solutions.

The optimum condition for obtaining a molybdenum wave is a pH of 4.5-5.5. At pH 1.5, there is obtained one wave whose height is only half of that obtained at pH 4.5-5.5 (Figure 4). All these facts indicate that reduction of molybdenum in the presence of Complexon I is a complicated one, in which there are intermediate stages at various pH values. Since the value of the diffusion current for molybdenum in the presence of Complexon I depends so strongly on the pH of the solution, a technique based on this Complexon is not expedient for quantitative determination of molybdenum.

Complexon III. Molybdate ions form a compound with Complexon III since, on addition of the latter to a molybdate solution, the half-wave potential shifts to more negative values (the pH of the solution was the same in both solutions). The nature of the polarogram obtained for molybdenum in the presence of Complexon III depends strongly on

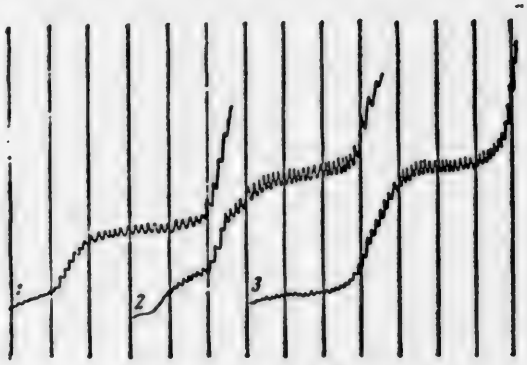

Fig. 4. Polarograms for $1.04 \cdot 10^{-3}$ M molybdate in 0.1 N buffer solution – 0.05 Complexon I solution, at various pH values: 1) pH 1.5; 2) pH 2.5; 3) pH 5.5

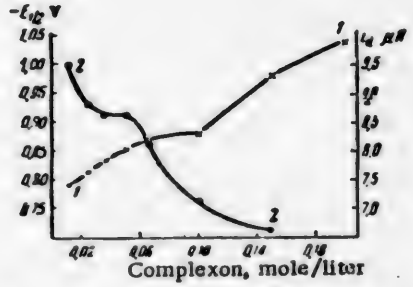

Fig. 5. Relation between the values of $E_{1/2}$ (Curve 1) and i_d (Curve 2) of molybdenum, and the concentration of Complexon III.

the pH, on Complexon III concentration, and on other factors.

In order to establish the influence of Complexon III concentration, various amounts of the latter were added to a $1.04 \cdot 10^{-3}$ M solution of molybdate in 0.1 N buffer solution. At Complexon III concentrations greater than 0.1 M, diffuse, extended waves are obtained; at concentrations below 0.1 M, clearly defined waves are obtained whose height is determined to some extent by the concentration. The half-wave potential shifts to more negative values with increasing Complexon III concentration. On Figure 5 is shown the relation between $E_{1/2}$ (Curve 1) and i_d (Curve 2) of molybdenum and Complexon III concentration. As can be seen from Figure 5, on the part of Curve 1 corresponding to Complexon III concentrations ranging from 0.06 to 0.1 M, the half-wave potential maintains a constant value of –0.87 volt; since the wave of the complex is

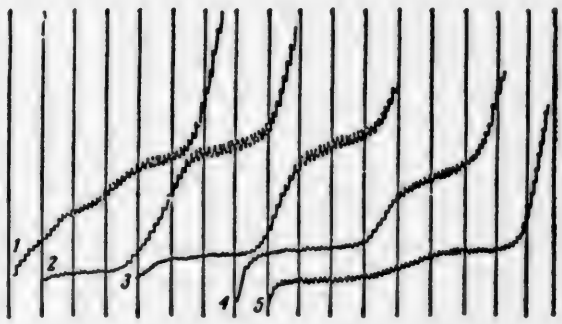

Fig. 6. Polarograms for $1.04 \cdot 10^{-3}$ M molybdate in 0.1 N acetate buffer – 0.065 M Complexon III at various pH values: 1) pH 2.45; 2) pH 4.22; 3) pH 6.70; 4) pH 7.51; 5) pH 8.32.

most clearly defined at a Complexon III concentration of 0.065 M, further work was carried out at this concentration.

TABLE 1

Relation Between the Limiting Current of Molybdenum and its Concentration ($m^{2/3} \cdot t^{1/6} = 2.00\ mg^{2/3} \cdot sec^{-1/2}$)

Mo concentration, in mmole/liter	i_d μa, obtained	$K = \frac{i_d}{cm^{2/3} \cdot t^{1/6}}$
1.042	9.091	4.35
0.521	4.695	4.50
0.261	2.597	4.97
0.208	2.098	5.04
0.156	1.798	5.76
0.104	1.199	5.78
0.052	6.616	5.91
0.021	0.250	5.95

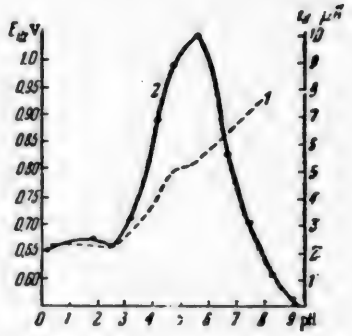

Fig. 7. Relation between the value of $E_{1/2}$ (Curve 1) and i_d (Curve 2) of molybdenum, and pH, in a supporting electrolyte of Complexon III (at pH<4, values of $E_{1/2}$ for the second wave are given).

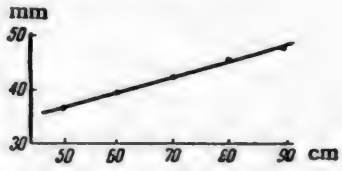

Fig. 8. Relation between wave height of molybdenum with Complexon III and the height of the mercury column (h).

In order to clarify the effect of pH, polarograms were obtained for a $1.04 \cdot 10^{-3}$ M solution of molybdate in a supporting electrolyte of 0.1 N acetate buffer – 0.065 M Complexon III at various pH values. It was found that at low pH values, there is obtained two step-like, extended waves; in the pH range 4-7, there is obtained one clearly-defined wave, whose half-wave potential and wave height depend to a lesser extent on pH. In alkaline solutions, the wave decreases sharply and, at a pH greater than 8, practically disappears completely (Figure 6). The relation between the half-wave potential and the value of the diffusion current, and pH is shown on Figure 7. As can be seen from Curve 1, the value of $E_{1/2}$ is constant in the limits pH 0-2.5; beyond this range, with increasing pH, the values of the half-wave potential shift strongly to negative values. The diffusion current increases with increasing pH (from pH 2.5), passes through a maximum at pH 5.5, drops again with increasing pH, and approximates to zero at pH about 9. Further work was accordingly carried out at this pH of 5.5.

In order to establish the nature of the limiting current obtained, polarograms were taken for $5.20 \cdot 10^{-4}$ M molybdate in a supporting electrolyte of 0.1 N buffer – 0.065 M Complexon III (pH 5.5), at various values of the height of the mercury column. As can be seen from Figure 8, the value of the limiting current of molybdenum depends on the height of the mercury column; accordingly, the limiting current is determined by diffusion.

The relation between the value of the limiting current and molybdenum concentration was investigated by taking polarograms of solutions containing different concentrations of molybdenum on a supporting electrolyte of 0.1 N acetate buffer – 0.065 M Complexon III with a pH of 5.5. The results obtained are given in Table 1.

As the results given in this table show, the constant of the molybdenum diffusion current changes with molybdenum concentration; it increases at lower molybdenum concentrations and remains practically constant in the concentration range 0.156-0.21 mmole/liter. For molybdenum concentrations up to $1.5 \cdot 10^{-4}$ M, the value of the constant corresponds to a process involving three electrons, i.e., to reduction of Mo^{VI} to Mo^{III}.

The slope of the current-voltage curve for molybdenum is considerably greater than the theoretical value, thereby indicating an irreversible character for the reduction process. Actually, on constructing a curve for $E - -\log \frac{i}{i_d - i}$, a value of 6 was found for $\underline{n}$, which should lead one to assume that reduction of Mo^{VI} to metal occurs. Such an assumption, of course, has no foundation in fact and consequently the process must be regarded as irreversible. In order to determine the number or electrons participating in the electrode reaction, a microcoulometric method proposed by Stromberg and Markacheva [12] was also used.

Numerous coulometric experiments also gave a value for $\underline{n}$ of about 5-6.

TABLE 2

Effect of Fe, Cu, Pb, Zn, V and W on the Values of the Limiting Current of Molybdenum in Complexon III as Supporting Electrolyte

Mo conc. in μg/ml	Concentration of added impurities, in μg/ml						Found i_d μa
	Fe	Cu	Pb	Zn	W	V	
5	—	—	—	—	—	—	0.45
5	5	—	—	—	—	—	0.46
5	25	—	—	—	—	—	0.45
5	50	—	—	—	—	—	0.38
100	—	—	—	—	—	—	9.01
100	100	—	—	—	—	—	7.49
100	500	—	—	—	—	—	6.16
100	1000	—	—	—	—	—	Not determined
5	—	5	—	—	—	—	0.45
10	—	—	—	—	—	—	0.90
10	—	50	—	—	—	—	0.80
100	—	100	—	—	—	—	6.83
100	—	500	—	—	—	—	5.99
5	—	—	5	—	—	—	0.47
5	—	—	25	—	—	—	0.47
5	—	—	50	—	—	—	0.63
5	—	—	—	50	—	—	0.46
5	—	—	—	—	50	—	0.46
100	—	—	—	—	—	100	8.83
100	—	—	—	—	—	1000	9.32

TABLE 3

Relation Between the Values of $E_{1/2}$ and i_d of Molybdenum in the Presence of Disodium Benzhydrylaminediacetate, and pH

Mo concentration, $M \cdot 10^{-4}$	pH	$-E'_{1/2}$ v	$-E''_{1/2}$ v	i'_d μa	i''_d μa
2.6	1.5	0.10	0.33	1.00	0.90
2.6	2.7	0.22	0.44	0.33	1.00
2.6	4.5	0.25	0.54	0.26	0.56
2.6	6.5	0.15	1.11	0.67	1.0
2.6	8.5-10.0	No wave		—	—

The influence of Fe^{III}, Cu, Pb, Zn, W, and V on the reduction wave of molybdenum in a solution of 0.1 N acetate buffer – 0.065 M Complexon III was also studied. The results obtained are given in Table 2.

It follows from Table 2 that iron, copper, and lead, when present in amounts which are ten times that of molybdenum, affect the polarographic determination of molybdenum in the presence of Complexon III. Tungsten, in amounts which are ten times those of molybdenum does not affect the height of the molybdenum wave. Vanadium only interferes at high concentrations of this element. Thus, by separating molybdenum from iron and copper, it can be determined in the presence of lead, zinc, and tungsten; this confirms the results obtained by Pribil and Blazek [11].

Other Complexons. Reduction of molybdenum in the presence of disodium benzhydrylamineacetate and disodium hexamethylenediaminetetracetate, synthesized by Lastovskii and co-workers [3], was also studied, as well as its reduction in the presence of cyclohexanediaminetetracetic acid.*

*Synthesized by M.N. Shchunkina in the Ordzhonikidze All-Union Scientific Research Chemical Pharmaceutical Institute.

TABLE 4

Relation Between the Values of $E_{1/2}$ and i_d for Molybdenum in the Presence of Hexamethylenediaminetetracetic Acid, and pH

Mo concentration, $M \cdot 10^{-4}$	pH	$-E_{1/2}$ v	i'_d μa
2.6	1.5	0.31	2.75
2.6	2.5	0.37	3.20
2.6	3.5	0.56	3.16
2.6	4.5	0.55	1.76
2.6	6.0-10	No wave	

TABLE 5

Relation Between the Values of $E_{1/2}$ and i_d for Molybdenum in the Presence of Cyclohexanediaminetetracetic acid, and pH (Mo concentration = $5.2 \cdot 10^{-4}$ M; Complexon concentration 0.05 M)

pH	$-E_{1/2}$ v	i_d μa
1.5	No wave	–
2.5	0.42	2.17
4.0	0.47	2.25
5.0	0.63	3.20
6.0	0.70	0.66
7.5-9.5	No wave	

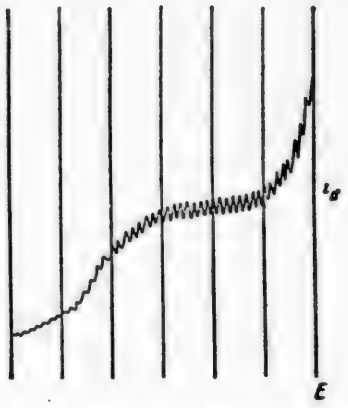

Fig. 9. Polarogram for molybdate in a supporting electrolyte of 0.1 N acetate buffer – 0.04 M hexamethylenediaminetetracetic acid – pH 2.5

Molybdenum in the presence of disodium benzhydrylaminediacetate gives very poorly defined, small waves in acid and neutral solutions only. The half-wave potential and the value of the diffusion current depend to a very large extent on the pH of the solution (Table 3).

On comparing Table 3 with Figure 7 it is clear that the diffusion current of molybdenum in the presence of Complexon III is several times greater than with the test complexon and, consequently, the latter has no advantages over Complexon III.

Molybdenum in the presence of hexamethylenediaminetetracetic acid gives one or two clearly defined waves in a 0.1 N acetate buffer, which is 0.05 M with respect to the complexon, according to the pH value. Table 4 contains results for the half-wave potentials and diffusion current of molybdenum as functions of the pH.

It should be noted that in acid solutions at all pH values, the molybdenum wave consists of two parts which are not clearly defined (Figure 9). Accordingly, the values of $E_{1/2}$ given in Table 4 are arbitrary values, since they are calculated on the basis of the whole wave.

It is, however, quite obvious from Table 4 that with increasing pH, the half-wave potential of molybdenum shifts to more negative values, while the diffusion current decreases, starting at pH 4.5. In solutions with pH 6, an extended curve is obtained which is difficult to measure, while at pH 8-10 there is no wave at all. On comparing the results obtained with those obtained for Complexon III, it is clear that hexamethylenediaminetetracetic acid has no advantages over Complexon III for the polarographic determination of molybdenum.

In the presence of cyclohexanediaminetetracetic acid, molybdenum, in a supporting electrolyte of 0.1 acetate buffer, is reduced on a dropping mercury cathode to give a clearly defined wave in acid solutions only, over a narrow pH range. The half-wave potential is dependent on pH (Table 5); in neutral and alkaline solutions no wave appears at all.

In strongly acid solutions (pH 1.5), no molybdenum wave is obtained, the complexon is precipitated under these conditions. With increasing pH the half-wave potential shifts to more negative values, while the diffusion current achieves a maximum value at pH 5. It follows from this that the optimum condition for reducing molybdenum is a buffer solution with a pH of 5. Nevertheless, on comparing the value of the diffusion current of molybdenum with this complexon, with that obtained with Complexon III, it is evident that it has no advantages over the latter.

SUMMARY

A study has been made of the reduction of molybdenum on a dropping mercury electrode in the presence of Complexon I, Complexon III, benzhydrylaminediacetic acid, hexamethylenediaminetetracetic acid, and cyclohexanediaminetetracetic acid.

It has been found that in all cases molybdenum is reduced in acid solutions. The half-wave potentials and the values of the diffusion currents are all strongly dependent on the pH value. No reduction waves of molybdenum are formed in alkaline solutions. It has been shown that Complexon III gives the best results from an analytical point of view.

Fe^{3+} and Cu^{2+} decrease the limiting current of molybdenum in the presence of Complexon III, while Pb, Zn, V, and W ions have practically no effect on the limiting current.

LITERATURE CITED

[1] M.V. Stackelberg, P. Klinger, W. Koch and E. Krath, Forschungsberichte Techn. Mitt. Krupp. Essen 2, 59 (1939).

[2] E.A. Kanevskii and L.A. Shvartsburd, Factory Labs. 9, 283 (1940).

[3] Ia.P. Gokhshtein, J.Gen. Chem. 10, 1725 (1940); Trans. Commission on Anal. Chem. 11 (V), 54 (1949).

[4] R. Höltje and R. Geyer, Z. anorg. Chem. 246, 243, 258 (1941).

[5] M.C. Johnson and R.J. Robinson, J. Anal. Chem. 24, 366 (1952).

[6] A.A. Vlcek, Chem. Listy 47, 1162 (1953).

[7] J.M. Kolthoff and E.P. Parry, J. Am. Chem. Soc. 73, 5315 (1951).

[8] F.A. Uhl, Z. anal. Chem. 110, 102 (1937).

[9] D.F. Boltz, Th. De Vries and M.G. Mellon, Anal. Chem. 21, 563 (1949).

[10] S.I. Siniakova and M.I. Glinkina, J. Anal. Chem. 11, 544 (1956).*

[11] R. Pribil and A. Blazek, Collection 16, 561 (1953).

[12] A.G. Stromberg and T.M. Markacheva, J. Phys. Chem. 28, 671 (1954).

[13] R.P. Lastovskii, Iu.I. Vainshtein, N.M. Diatlova, V.Ia. Temkina and I.D. Kolpakova, J. Anal. Chem. 10, 128 (1955).*

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THE SOLUBILITY OF COPPER AND SILVER REINECKE ACID SALTS

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Ammonium tetrathiocyanatoaminochromiate (Reinecke's salt) is widely used in analytical chemistry for the detection and determination of a number of metals, for example, for the spot and fractional detection of copper [1], and also for its gravimetric and titrimetric determination [2, 3], for the quantitative determination of mercury [4, 5], cadmium [4, 7], and thallium [6].

Despite the fact that Reinecke's salt has been known for a long time as an analytical reagent for the isolation from solution of copper, mercury, thallium, silver, and other metals, hitherto there has been no published data available on the solubility of the Reineckates of these metals.* In the meantime, a knowledge of the values of the solubility products of these compounds would enable analysts to be in a better position to solve questions related to the development of methods for detecting and determining a number of metals. The object of the work described in the present article was the determination of the solubilities of the Reineckates of copper and silver.

Reagents and Materials

Reinecke salt containing radioactive chromium-51 (a γ-radiator with a half-life period of 26.5 days), as well as Reinecke salt containing nonradioactive chromium were used in the present investigation.

The Reineckate of univalent copper containing radioactive chromium-51, and silver Reineckate containing the radioactive isotope of this element (a β-emitter with a half-life period of 225 days) were prepared.

Synthesis of Reinecke's salt. The Reinecke salt was prepared by the method described by Kul'berg [10]. For synthesizing Reinecke salt containing radioactive chromium, the nitrate and sulfate, and also the trioxide of chromium were used. The nitrate or sulfate of radioactive chromium were converted beforehand into ammonium dichromate by boiling with an ammoniacal solution of hydrogen peroxide.

Synthesis of copper Reineckate. To 200 ml of a 1 N solution of $CuCl_2$ acidified with 5-10 ml of concentrated HCl, and heated to the boiling point, was added a few small portions, 0.2 g each, of hydrazine hydrochloride until the solution was completely colorless. To the reduced solution at a temperature of 70° was added dropwise a saturated solution of Reinecke's salt acidified with hydrochloric acid, until formation of a precipitate ceased and a stable red color was obtained. This solution was then cooled by continuous agitation. The precipitate was filtered through a No. 4 filter and washed on the filter, first with 5% hydrochloric acid, and then with hot distilled water. Finally, the precipitate was washed with alcohol, and then with ether, and dried in a desiccator over sulfuric acid.

Synthesis of silver Reineckate. Active metallic silver-110 was dissolved on heating in nitric acid; to this solution was added an inactive solution of silver nitrate. This mixture was carefully evaporated to dryness and then dissolved in distilled water to give a 0.2 N solution. To a freshly prepared 0.08% N solution of Reinecke's salt (free from active chromium) was added a small excess of the solution of $AgNO_3$ described above. A large excess of $AgNO_3$ should be avoided, otherwise a flocculent precipitate which is difficult to filter will be formed.

*After the present article had been sent to the J. Anal. Chem., we became aware of the article by Bagbanly on the solubilities of these salts [13].

The precipitate of $Ag[Cr(NH_3)_2(SCN)_4]$ obtained was filtered off and washed in a centrifuge until the washings no longer gave a reaction for NO_3^- ions (test with diphenylamine). It was then dried in a desiccator over sulfuric acid and analyzed.

Determination of the Solubility of Copper Reineckate

During the study of the solubility of copper Reineckate we bore in mind the fact that at infinite dilution, normal concentration and active concentration become equal [11]. The low solubility of copper Reineckate enables one to use the Nernst equation for calculating the solubility product.

The method used for determining the solubility was as follows. A sample of test material (0.05-0.12 g) was placed in the vessel to be used for the solubility determinations; this vessel was provided with stirrers, and kept in a thermostat. Distilled water or 0.01 N hydrochloric acid was then added. Saturation was reached after 10-12 hours. Samples were withdrawn by means of a pipet fitted with a filter disc made from Schott No. 1 or by filtration through a fine filter paper.

Copper was deposited from the filtrate by means of cadmium sulfide. The copper sulfide precipitate plus filter were washed, and converted first into the cupric oxide, and then into the sulfate. Copper was determined iodometrically in the sulfate by titration with 0.02 N sodium thiosulfate, using a microburet.

TABLE 1

Solubility and Solubility Product of Copper Reineckate at 15°

	Solubility of the salt, in mole/liter		Solubility product in aqueous solution
	in pure water	in 0.01 N HCl	
	$5.98 \cdot 10^{-5}$	$6.65 \cdot 10^{-5}$	$3.58 \cdot 10^{-9}$
	$6.20 \cdot 10^{-5}$	$6.40 \cdot 10^{-5}$	$3.84 \cdot 10^{-9}$
	$6.00 \cdot 10^{-5}$	$7.31 \cdot 10^{-5}$	$3.60 \cdot 10^{-9}$
Mean	$6.6 \cdot 10^{-5}$	$6.78 \cdot 10^{-5}$	$3.67 \cdot 10^{-9}$

Results for the determination of the solubility of copper Reineckate in water and in 0.01 N HCl at 15° are given in Table 1. The same table also contains the results for the solubility product.

The solubility of copper Reineckate in pure water ($6.6 \cdot 10^{-5}$ mole/liter) differs very little from the solubility of this salt in 0.01 N hydrochloric acid ($6.78 \cdot 10^{-5}$ mole/liter). This fact justifies the technique used for determination of small amounts of copper by precipitation of it as the Reineckate from weak hydrochloric acid solutions.

The results given in Table 1 are in good agreement with the results obtained by the radiochemical method.

Determination of the Solubilities of the Reineckates of Copper and Silver by the Method of Labelled Atoms*

The method used for the determination of sparingly soluble salts has been described several times in the literature.

500 mg of $Cu[Cr(NH_3)_2(SCN)_4]$ labelled with chromium-51 or $Ag[Cr(NH_3)_2(SCN)_4]$ labelled with silver-110, was placed in the vessel used for determination of the solubility, and 500 ml of distilled water added; the mixture was then held in a thermostat at 15°.

Saturation was reached after continuous stirring for 8-10 hours in the case of copper Reineckate and 30-32 hours in the case of silver Reineckate.

50 ml of the solution was taken by means of a pipet with a filter plug (made from Schott No. 4 filter) and transferred to a Petrie dish. The weight of solution was determined; it was then evaporated to dryness under an infra-red lamp.

*E.A. Popovkina and V.V. Pushkarev participated in this work.

In order to prepare a standard, 0.1 g of copper Reineckate was dissolved in 50 ml of 10% HCl containing a small amount of concentrated HNO_3. The standard silver Reineckate was prepared in the same way but, in this case, nitric acid was used as the solvent. The standard solutions were also evaporated in the same way in Petrie dishes of the same size. A Type B counter with a torsion counter was used for determining the activity. During determination of the specific activity, the error resulting from insufficient evenness of the layer of deposit on the bottom of the Petrie dish was eliminated by rotating the dish through 360° at 90° intervals.

The activity of the sample taken for determination of the solubility was determined in the same way; it amounted to, on an average, about 300 impulses/minute in the case of copper Reineckate, and to 450 impulses/minute for silver Reineckate. The background intensity did not exceed 40-45 impulses/minute.

The results obtained are given in Table 2.

TABLE 2

Solubility of Copper and Silver Reineckates at 15°

Formula of test material	Solubility, in mole/liter	Indicator
$Cu[Cr(NH_3)_2(SCN)_4]$	$4.75 \cdot 10^{-5}$	Chromium-51
$Ag[Cr(NH_3)_2(SCN)_4]$	$1.71 \cdot 10^{-7}$	Silver-110

The results obtained for the solubility of copper Reineckate by means of the radioactive indicator method are very similar to those obtained by the method described above (Table 1).

A study of the composition of the bottom phases for their copper content by chemical analysis showed that they had not changed as the result of the action of water.

In conclusion, we should like to thank E.L. Krylov for his valuable advice.

SUMMARY

The solubility of copper and silver Reineckates in water at 15° has been studied. It has been found that the solubility of these salts decreases with increasing atomic weight of the test element. The solubility product of copper Reineckate at 15° has been calculated.

LITERATURE CITED

[1] A. Reinecke, Ann. 126, 113 (1863).

[2] C. Mhar, Z. anorg. Chem. 225, 386 (1935).

[3] I.L. Bagbanly, Bull. Azerbaidzhan Acad. Sci. SSR 5, 11, 81 (1946); 6, 88 (1947).

[4] A.M. Dymov and A.M. Shchelkunova, Factory Labs. 20, 270 (1954).

[5] C. Mhar, Ang. Chem. 53, 257 (1940); Z. anal. Chem. 104, 241 (1936).

[6] A.A. Saukov, Proc. Acad. Sci. USSR 20, 375 (1938).

[7] O.A. Songina, Sci. Trans. Kazakh. University 16, 1954, p. 58.

[8] I.L. Bagbanly, Proc. Acad. Sci. Azerbaidzhan SSR 9, 373 (1953).

[9] N.T. Voskresenskaia, J. Anal. Chem. 10, 222 (1955).•

[10] L.M. Kul'berg, Syntheses of Organic Reagents••(Goskhimizdat, 1947), p. 123.

[11] A.F. Kapustinskii, J. Appl. Chem. 16, 50 (1943).

[12] Radiochemistry•• Collection of Articles (Izd. MGU, 1952), pp. 91 and 99.

[13] I.L. Bagbanly, Proc. Acad. Sci. Azerbaidzhan SSR 12, 459 (1956).

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DETERMINATION OF SMALL AMOUNTS OF INDIUM BY A TITRIMETRIC AND PHOTOMETRIC METHOD

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One of the few methods which have been published hitherto for the titrimetric determination of indium is based on potentiometric titration of indium by means of potassium ferrocyanide [1]. The compound formed has been ascribed the formula $KIn_3[Fe(CN)_6]_4$. Kolthoff [2] in describing this method notes, however, that "the composition of the precipitate which is formed has not yet been studied." During studies of systems including indium chloride and the ferrocyanides of lithium, sodium, potassium, rubidium, and cesium [3, 4], it was found that in their capacity to form sparingly soluble mixed ferrocyanides with indium, the alkali metals can be arranged in the following ascending order: Li < Na < K < Rb < Cs (Table 1).

TABLE 1

The Mixed Ferrocyanides of Indium and the Alkali Metals

Ferrocyanides of the alkali metals	$Li_4[Fe(CN)_6]$ $Na_4[Fe(CN)_6]$	$K_4[Fe(CN)_6]$	$Rb_4[Fe(CN)_6]$	$Cs_4[Fe(CN)_6]$
Composition of the solid phases formed in the systems: $InCl_3-Me_4[Fe(CN)_6]-H_2O$	$In_4[Fe(CN)_6]_3$	1) $In_4[Fe(CN)_6]_3$ 2) $KIn[Fe(CN)_6]$	1) Phase of variable composition: $In_4[Fe(CN)_6]_3 \times$ $\times Rb_4[Fe(CN)_6]$ $(x < 1)$ 2) $RbIn[Fe(CN)_6]$	1) $CsIn[Fe(CN)_6]$ 2) Phase of variable composition: $CsIn[Fe(CN)_6] \times$ $\times xCs_4[Fe(CN)_6]$ $(x < 1/4)$ 3) $Cs_7In_5[Fe(CN)_6]_6$

The work carried out, despite the complexity of the reactions which occur, allowed conclusions to be drawn which could be useful from an analytical point of view.

In the light of the results which we obtained, it is completely obvious that the reason for the inaccuracy of the potentiometric method indicated above, is the variable composition of the precipitate formed thus, for a ratio of $K_4[Fe(CN)_6]:InCl_3 = 0.75$ in the original mixture, the normal ferrocyanide of indium is formed, which then reacts with $K_4[Fe(CN)_6]$ to form a mixed salt $KIn[Fe(CN)_6]$, as a result of which the potential change observed is not clearly defined.

The only compound which has a definite composition is formed when indium ions react with lithium and sodium ferrocyanides. The equivalence point during potentiometric titration is observed, in this case, at ratios of the components corresponding to the formation of $In_4[Fe(CN)_6]_3$.

From what has been said above, it follows that for the analytical determination of indium, the ferrocyanides of lithium and sodium should have preference over those of potassium, rubidium, and cesium. Accordingly, in our subsequent work on the titrimetric determination of indium, we used sodium ferrocyanide as being the most readily available and cheapest reagent.

Titrimetric Determination of Indium

A high resistance potentiometer type PPTV 1 was used for potentiometric titration in conjunction with a galvanometer with a shadow scale. A saturated calomel electrode was used as the standard half-element. The indicator electrode was a platinum one. The salt bridge was a saturated KCl solution.

TABLE 2

Potentiometric Titration of $InCl_3$ by Means of $Na_4[Fe(CN)_6]$

$InCl_3$ 40 ml 0.00547 *M*			$InCl_3$ 40 ml 0.01 *M*		
$Na_4[Fe(CN)_6]$ 0.0328 *M*	emf, in mv	$\frac{Na_4[Fe(CN)_6]}{InCl_3}$	$Na_4[Fe(CN)_6]$ 0.0328	emf, in mv	$\frac{Na_4[Fe(CN)_6]}{InCl_3}$
0 2	0.333	0.03	2.0	0.387	0 16
			4 0	0.399	0.33
1.0	0.387	0.15	6.0	0.420	0.49
			7.0	0.450	0.57
1.6	0.416	0.24	7.4	0.480	0.61
2.0	0.456	0.30	7.8	0.500	0.64
			8.2	0.500	0.67
3.0	0.479	0.45	8.9	0.550	0.73
3.8	0.489	0.57	9.0	0.550	0.74
4.0	0.489	0.60	9.05	0.570	0.74
4.4	0.489	0.66	9.10	0.590	0.74
4.8	0.537	0.72	9.15	0.615	0.75
5.0	0.537	0.75	9.20	0.350	0.75
5.2	0.270	0.78	9.25	0.300	0.76
5.4	0.200	0.81	9.30	0.252	0.76
6.0	0.135	0.90	9.50	0.201	0.78

TABLE 3

Titration of Indium With a Solution of $Na_4[Fe(CN)_6]$

In^{3+} taken, in g	In^{3+} found, in g
0.0010	0.0010
0.0017	0.0016
0.0026	0.0026
0.0034	0.0035
0.0050	0.0050
0.0068	0.0067
0.0085	0.0087
0.0100	0.0103
0.0200	0.0190
0.0400	0.0400
0.1000	0.0990

TABLE 4

Titration of Indium With a Solution of $Na_4[Fe(CN)_6]$ in the Presence of Various Salts and Acids

Taken			Found
impurity, in g		In^{3+}, in g	In^{3+}, in g
NaCl	0.5	0.010	0.010
NH_4Cl	0.5	0.010	0.010
Na_2SO_4	0.5	0.010	0.010
$(NH_4)_2SO_4$	0.5	0.010	0.010
Tartaric acid	3	0.010	0.013
Oxalic acid	3	0.010	0.0087
Citric acid	3	0.010	0.010
Phosphoric acid	3	0.010	0.002

During titration of indium chloride solutions of varying concentrations with sodium ferrocyanide, as is evident from Table 2, there was observed a potential jump at the point corresponding to a ratio of $Na_4[Fe(CN)_6]:InCl_3 = 0.75$, i.e., when formation of a precipitate of $In_4[Fe(CN)_6]_3$ was complete. An increase in acid concentration has a deleterious effect on the titration, in that it smooths out the potential jump.

We tried to use diphenylamine as the indicator for the titration of indium with a solution of $Na_4[Fe(CN)_6]$. Diphenylamine in acid solution, under the effect of an oxidizing agent, changes into colorless diphenylbenzidene and is then oxidized to violet diphenylbenzidene [5]. In strongly acid solutions, some of the diphenylbenzidene may be oxidized further, before all the diphenylamine has been converted into diphenylbenzidene.

Titration of indium in the presence of acetic, hydrochloric, nitric, and sulfuric acids, showed that sulfuric acid is the most suitable for titration. A stable, and fairly intense color develops in the course of two to three

minutes in 5% H_2SO_4. Titration should be carried out in the cold.

The results obtained (Table 3) show that determination of indium by this method is accurate enough. The best results are obtained on titrating 0.02-0.005 g of indium in 50 ml of solution.

Results for titration of indium in synthetic mixtures of a complex nature, which are met with in various cases of analytical chemistry, are given in Tables 4 and 5. As these results show, the presence of small amounts of chlorides and sulfates in solution does not interfere with titration, but the indicator color develops considerably slower (five to ten minutes). Oxalic acid, when present, depresses the color intensity somewhat; phosphoric acid interferes.

TABLE 5

Titration of Indium With a Solution of $Na_4[FE(CN)_6]$ in the Presence of Various Cations (Original Volume 25 ml)

2.5 mg of the chlorides or sulfates taken in each case							In^{3+} taken, in mg	In^{3+} found, in mg
Be	Ca	Mg	Mn	Al	Ga	La	2.5	2.6
Be	Ca	Mg	Mn	Al	Ga	La	5.0	5.3
Be	Ca	Mg	Mn	Al	Ga	La	10.0	10.0
Be	Ca	Mg	Mn	Al	Ga	La	15.0	15.0
Cd	Mo	U	Tl	Th			5.0	5.0
Cd	Mo	U	Tl	Th			5.0	5.2
Co	Ni	Zn					5.0	5.2
V							5.0	5.1
Ge							5.0	5.1

The presence in solution of many cations (in the form of their chlorides and sulfates) has no effect on titration. Chromium, tungsten, copper, and large amounts of iron interfere.

Zinc, cobalt, aluminum, and tin also give a color in the presence of diphenylamine, but their deleterious influence was successfully eliminated by addition of 3 to 5 g of citric acid to 50 ml of the test solution.

Taking into account the facts given above, the following technique was developed for determining indium by means of $Na_4[Fe(CN)_6]$.

To 50 ml of a solution of an indium salt in 5% sulfuric acid is added 2 drops of a 1% solution of potassium ferricyanide and 2 drops of 1% diphenylamine in concentrated sulfuric acid. In the presence of materials which interfere, 5 g of citric acid is added, and the solution titrated in the cold with $Na_4[Fe(CN)_6]$ solution until the color disappears in the course of 30 seconds; in the presence of cobalt, nickel, zinc, germanium, and vanadium, titration should be carried out to the first decolorization of the solution. The concentration of $Na_4[Fe(CN)_6]$ is checked by titration with potassium permanganate.

Photometric Determination of Indium

The intensity of the color which develops on addition of potassium ferricyanide and diphenylamine to the diluted solution of indium is proportional to the indium concentration. On this basis a photometric determination of small amounts of indium was carried out. The most favorable medium for photometric measurements is 5% H_2SO_4. Results for determination of indium are given in Tables 6 and 7.

As the results obtained show, the minimum amount of indium which can be determined by means of the recommended method is $4 \cdot 10^{-5}$ g in 25 ml of solution. The method can be used for the determination of indium in the presence of Be, Ca, Mg, La, Cd, Ga, Tl, U, Th, Al, Co, Ni, Zn and Mn.

In the presence of zinc, the color of indium develops immediately and is considerably more intense; after ten minutes, however, it corresponds to that of the standard.

The amount of indium found, as is evident from Table 7, in most cases corresponds to the amount taken.

TABLE 6

Photometric Determination of Indium (Volume of solution 25 ml)

In^{3+} taken, in mg	In^{3+} found, in mg	In^{3+} taken, in mg	In^{3+} found, in mg
0.04	0.04	1.0	1.0
0.1	0.1	1.4	1.4
0.2	0.2	2.0	2.0
0.3	0.3	3.0	2.8
0.4	0.38	4.0	3.8

TABLE 7

Photometric Determination of Indium in the Presence of Impurities (In^{3+} taken, 0.25 mg in 25 ml)

Content of impurity in 25 ml of solution, in mg	In^{3+} found, in mg	Content of impurity in 25 ml of solution, in mg	In^{3+} found, in mg
Be – 2.5	0.25	Th – 2.5	0.25
Ca – 2.5	0.25	Al – 2.5	0.23
Mg – 2.5	0.25	Co – 1.0	0.27
Mn – 2.5	0.25	Ni – 2.5	0.25
La – 2.5	0.25	Zn – 2.5	0.27
Cd – 2.5	0.25	V – 2.5	0.25
Ga – 2.5	0.25	Mo – 2.5	0.25
Ti – 2.5	0.25	Ge – 2.5	0.25
U – 1.0	0.25		

The deviations sometimes observed are insignificant when one bears in mind that impurities are present and the amount of indium is small. Cr, Ni, Cu, Fe, and Tl interfere with indium determination.

For the photometric determination of indium, one drop of a 1% aqueous solution of potassium ferrocyanide is added to the solution of the indium salt; this is followed by one drop of a 1% solution of diphenylamine in concentrated sulfuric acid. After five to ten minutes, the color obtained is compared with those of a series of standards prepared under the same conditions. In the presence of impurities, 3-5 g of citric acid is added to both the test and standard solutions. In the presence of cadmium, cobalt, zinc, and uranyl, the color should be compared with that of the standard after 8-10 minutes.

SUMMARY

A titrimetric method is proposed for the determination of indium by means of $Na_4[Fe(CN)_6]$; the method is based on the formation, during titration, of a precipitate of the normal ferrocyanide of indium $In_4[Fe(CN)_6]_3$.

A photometric method has been developed for the determination of small amounts of indium by means of a mixture of $K_3[Fe(CN)_6]$ and diphenylamine.

LITERATURE CITED

[1] U.B. Bray and H.D. Kirschmann, J. Am. Chem. Soc. 49, 2739 (1927).

[2] I.M. Kolthoff and V.A. Stenger, Volumetric Analysis* (Goskhimizdat, 1950), Vol. 2, p. 377.

*In Russian.

[3] E.N. Deichman and L.V. Tananaev, Chemistry of Rare Elements 2, 1955, p. 37.

[4] E.N. Deichman, Bull. Acad. Sci. USSR, div. chem. sci. 9, 1013 (1957).•

[5] J.M. Kolthoff and L.A. Sarver, Z. Elektrochem. 36, 139 (1930).

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SEPARATION OF THORIUM FROM THE RARE EARTHS BY MEANS OF PYRIDINE AND PYRIDINE NITRATE

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In a previous article [1] we showed that it is possible to separate thorium quantitatively from manganese, nickel, cobalt, copper, zinc, and cadmium by means of pyridine. Naturally, the question arises as to whether or not it is possible to separate thorium from the rare earths. The behavior of the latter toward pyridine has only been studied to a very limited extent. Jefferson [2], without adducing any definite proof, notes the quantitative precipitation of cerium (the valency of cerium is not given) and the incomplete precipitation of lanthanum, neodymium, and praseodymium. Watters and Kolthoff [3] point out that quadrivalent cerium is quantitatively coprecipitated with ferric hydroxide during precipitation with pyridine. Trivalent cerium is quantitatively coprecipitated with ferric hydroxide under conditions where the amount of ferric oxide is four times that of the cerium. In the method we have described for precipitation of metal hydroxides by means of pyridine [4], the pH was established at about 6.5.

The pH values at which the hydroxides of some of the metals we were interested in, according to Britton's results [5], are given in Table 1. It might be assumed that during separation of the hydroxides by means of pyridine, when the solution has a pH of about 6.5, precipitation of the rare-earth hydroxides is not quantitative. It was necessary to check our assumptions carefully; in addition, it was desirable to find conditions whereby differences in the pH values at which the hydroxide of thorium and the hydroxides of the rare earths separate out could be used for the quantitative separation of thorium from these elements.

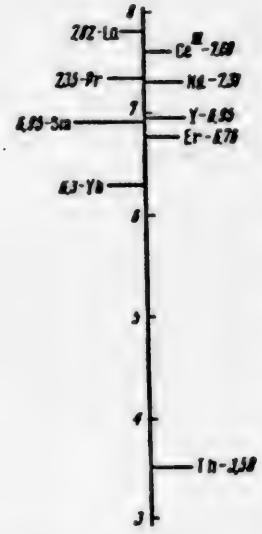
For these experiments, solutions of thorium nitrate and of the nitrates of the rare earths were prepared; these included the nitrates of cerium, yttrium, lanthanum, neodymium, praseodymium, erbium, samarium, and ytterbium; the solutions were standardized gravimetrically.

On carrying out the deposition of rare-earth hydroxides by means of pyridine under the usual conditions, i.e., by heating in the presence of about 6 g ammonium nitrate or chloride, it was found that about 50% was precipitated. Precipitation by means of pyridine in the absence of ammonium salts, although it led to a greater percentage precipitation, nevertheless did not yield quantitative results.

In order that during precipitation of thorium hydroxide the hydroxides of the rare earths were not precipitated, it was found necessary to lower the concentration of OH^- ions, i.e., to lower the pH of the solution, but nevertheless the pH still had to be kept within certain limits to ensure complete precipitation of thorium hydroxide. It was found most expedient to use pyridine in the presence of pyridine nitrate. As shown already [6, 4], such a solution permits accurate regulation of the pH of the medium during precipitation, and gives a pH of about 4.1-4.2.

The precipitation reagent – a solution of pyridine mixed with its nitrate – was prepared as follows: to 20 ml of distilled nitric acid sp.gr. 1.32-1.33 (or 15 ml of nitric acid sp.gr. 1.40) measured out from an accurate cylinder, was added an approximately equal volume of water; this was followed by 34 ml of pyridine which was thoroughly mixed in; the solution was finally made up to 100 ml with water.

Preliminary experiments showed that it is desirable to precipitate thorium in the presence of ammonium nitrate which favors the formation of a denser precipitate of thorium hydroxide, and favors rapid settling out of such precipitates. 6 g of ammonium nitrate was added to the solution of thorium nitrate and the volume made up to about 100 ml with water; the solution was then heated to 80°. The solution was neutralized with 10% am-



pH values at which various hydroxides separate out according to Britton.

monia solution, the latter being added dropwise with constant agitation until a weak turbidity appeared. 5-6 drops of nitric acid sp.gr. 1.4 was then added, and the solution stirred to get rid of the turbidity; the liquid was then brought to the boil and, having removed the beaker from the source of heat, thorium hydroxide was precipitated by adding 15 ml of the reagent mentioned above dropwise from a dropping funnel, with constant agitation. Having covered the beaker with a watch glass, the solution was again brought to incipient boiling and, having removed the beaker from the source of heat, it was transferred to a boiling-water bath for the precipitate to coagulate and settle down; it was left there for 30 minutes.

The precipitate was filtered off, washed a few times with hot 3% ammonium nitrate containing a small amount of the precipitation reagent (5 ml of reagent to 100 ml of the 3% ammonium nitrate). The filter paper plus precipitate were then dried and ashed in a porcelain crucible; the residue was finally calcined in an electric oven until the thorium dioxide obtained was of constant weight.

The experimental results (Table 1) show that thorium is removed quantitatively when the conditions indicated are used. As noted already, the pH of the solution was maintained at approximately 4.1-4.2 during the precipitation.

Since the thorium hydroxide is precipitated in a very dense form, while the pH maintained during precipitation is fairly low, one would expect that in such a way it should be possible to separate thorium from the rare earths. We mixed a solution of a thorium salt with a solution of a salt of one of the rare earths and carried out precipitation as described above. The thorium hydroxide precipitate was washed very carefully.

TABLE 1

(Volume of Solution about 120 ml)

ThO_2 taken, in g	ThO_2 found, in g	Error in ThO_2, in g	ThO_2 taken, in g	ThO_2 found, in g	Error in ThO_2, in g
0.0010	0.0011	+0.0001	0.0102	0.0104	+0.0002
0.0010	0.0010	±0.0000	0.0512	0.0512	±0.0000
0.0051	0.0050	−0.0001	0.0512	0.0510	−0.0002
0.0051	0.0053	+0.0002	0.1024	0.1022	−0.0002
0.0102	0.0101	−0.0001	0.1024	0.1025	+0.0001

TABLE 2

(Volume of Solution about 120 ml)

Taken, in g		ThO_2 found, in g	Error in ThO_2, in g	Taken, in g		ThO_2 found, in g	Error in ThO_2, in g
ThO_2	Ce_2O_3			ThO_2	Ce_2O_3		
0.0010	0.1010	0.0010	±0.0000	0.0512	0.0050	0.0512	±0.0000
0.0010	0.1010	0.0009	−0.0001	0.1024	0.0010	0.1023	−0.0001
0.0051	0.0505	0.0049	−0.0002	0.1024	0.0010	0.1024	±0.0000
0.0051	0.0505	0.0052	+0.0001	0.1024	0.0005	0.1025	+0.0001
0.0102	0.0101	0.0103	+0.0001	0.1024	0.0005	0.1024	±0.0000
0.0102	0.0101	0 0101	−0.0001	0.1024	0.1010	0.1025	+0.0001
0.0512	0.0050	0.0511	−0.0001	0.1024	0.1010	0.1023	−0.0001

Table 2 contains the results obtained during separation of thorium from cerium. The amount of thorium dioxide obtained after calcining the hydroxides precipitated, differed only very insignificantly from the amounts taken. The deviations in weight did not exceed the normal errors of weighing. The thorium oxide was pure

white in color. In order to check for small amounts of cerium in the precipitated thorium oxide, the latter was fused with sodium pyrosulfate and, after leaching with dilute sulfuric acid, the hydrogen peroxide test for cerium was applied. No cerium was found in any of the tests.

Table 3 contains the results obtained during separation of thorium from other rare earths. Variations in the weight of thorium dioxide were found to be negligible also during separation of thorium from yttrium and lanthanum. The thorium dioxide obtained was pure white in color; in these cases, however, the white color could not be used for assessing the purity of the thorium dioxide since yttrium and lanthanum oxides are also white in color. A spectroscopic examination of the thorium dioxide for the presence of small amounts of yttrium and lanthanum showed that the amount of both yttrium and lanthanum oxides did not exceed 0.0001 g. During separation of thorium from neodymium and praseodymium, errors in the determination of thorium did not exceed weighing errors. The thorium oxide was again white in color. The latter indicates a high degree of purity for the thorium dioxide, since (as tests showed) the presence of 0.0001 g of neodymium or praseodymium oxide in 0.05 g of thorium dioxide was sufficient to give a clearly discernible color. Accordingly, if the thorium hydroxide traps neodymium or praseodymium to any extent during precipitation, the amounts of the latter involved must be less than 0.0001 g. During separation of thorium from erbium, samarium, and ytterbium, the amounts of thorium dioxide actually found deviated very insignificantly from the expected amounts, and the errors involved were very small. The thorium dioxide obtained was pure white in color, indicating that contamination by erbium oxide (if there was any there) was negligible. Less than 0.0001 g of ytterbium could be found spectroscopically, while samarium could not be detected.

TABLE 3

(0.0512 g of ThO_2 taken)

Amount of rare-earth oxide added, in g		ThO_2 found, in g	Error in g ThO_2	Amount of rare-earth oxide added, in g		ThO_2 found, in g	Error in g ThO_2
Y_2O_3—	0.0051	0.0511	−0.0001	Pr_2O_3	0.0537	0.0514	+0.0002
	0.0051	0.0512	±0.0000		0.1074	0.0513	+0.0001
	0.0510	0.0513	+0.0001		0.1074	0.0512	±0.0000
	0.0510	0.0512	±0.0000	Er_2O_3—	0.0050	0.0513	+0.0001
	0.1020	0.0511	−0.0001		0.0050	0.0511	−0.0001
	0.1020	0.0513	+0.0001		0.0502	0.0513	+0.0001
La_2O_3—	0.0050	0.0513	+0.0001		0.0502	0.0510	−0.0002
	0.0050	0.0511	−0.0001		0.1004	0.0511	−0.0001
	0.0501	0.0513	+0.0001		0.1004	0.0511	−0.0001
	0.0501	0.0510	−0.0002	Sm_2O_3—	0.0050	0.0513	+0.0001
	0.1002	0.0512	±0.0000		0.0050	0.0512	±0.0000
	0.1002	0.0513	+0.0001		0.0498	0.0512	±0.0000
Nd_2O_3—	0.0051	0.0512	±0.0000		0.0498	0.0513	+0.0001
	0.0051	0.0514	+0.0002		0.0996	0.0512	±0.0000
	0.0510	0.0512	±0.0000		0.0996	0.0511	−0.0001
	0.0510	0.0510	−0.0002		0.0047	0.0511	−0.0001
	0.1020	0.0511	−0.0001	Yb_2O_3 –	0.0047	0.0512	±0.0000
	0.1020	0.0511	−0.0001		0.0473	0.0510	−0.0002
Pr_2O_3—	0.0054	0.0513	+0.0001		0.0473	0.0513	+0.0001
	0.0054	0.0513	+0.0001		0.0946	0.0511	−0.0001
	0.0537	0.0511	−0.0001		0.0946	0.0512	±0.0000

It is evident, therefore, that even one precipitation of thorium hydroxide by means of a reagent consisting of a mixture of pyridine and pyridine nitrate makes it possible, under the conditions indicated, to carry out a practically complete separation of thorium from the rare earths.

Since, in certain cases, the rare earths taken individually behave somewhat differently than when they are taken together, we decided to carry out a series of tests on the separation of thorium from mixtures of rare earths. The experimental conditions used were the same as before.

As is evident from Table 4, the errors involved during determination of thorium dioxide were very insignificant. The thorium dioxide was pure white in color; no cerium could be detected in it by chemical means. Spectroscopic examination gave the following results: yttrium oxide – less than 0.0001; lanthanum oxide – less than 0.0001; ytterbium oxide – less than 0.0001; samarium oxide – not detected. The pure white color of the

TABLE 4

The Following Amounts were Taken: 0.0202 g Ce_2O_3, 0.0204 g Y_2O_3, 0.0200 g La_2O_3, 0.0204 g Nd_2O_3, 0.0214 g Pr_2O_3, 0.0200 g Er_2O_3, 0.0200 g Sm_2O_3 and 0.0207 g Yb_2O_3

ThO_2 taken, in g	ThO_2 found, in g	Error in ThO_2, in g
0.0512	0.0513	+0.0001
0.0512	0.0511	−0.0001
0.1024	0.1022	−0.0002
0.1024	0.1024	±0.0000

thorium dioxide showed that contamination by neodymium and praseodymium (if they were there at all) was negligible and less than 0.0001 g.

Experimental procedure. Usually, thorium, cerium and the rare earths are isolated as their oxalates, which by careful calcination are converted into the oxides. The mixture of oxides is dissolved on heating in nitric acid sp.gr. 1.5; the solution is evaporated in a porcelain dish on a water bath to dryness, a few drops of alcohol being added to convert cerium to the trivalent form. The residue is moistened with a small amount of nitric acid, some water is then added and the whole thoroughly mixed. Thorium is removed as the hydroxide from the solution obtained, as follows.

The solution is diluted with water so that 100 ml of solution contains not more than 0.2 g of thorium dioxide. To about 100 ml of the solution is added 6 g of chemically pure ammonium nitrate, and the solution heated to 80°, after which it is neutralized with 10% ammonia solution, the latter being added dropwise, with constant agitation, until a slight turbidity appears. Five to six drops of nitric acid sp.gr. 1.4 is then added to remove the turbidity. The liquid is next brought to the boil and, having removed the beaker from the source of heat, thorium is precipitated as the hydroxide by adding dropwise from a dropping funnel, with careful agitation, 15 ml of reagent consisting of the mixture of pyridine and pyridine nitrate.

The beaker is covered with a glass and the solution again heated to incipient boiling and, having removed the beaker from the source of heat, it is transferred to a boiling-water bath for the precipitate to coagulate and settle out over a period of 30 minutes. The precipitate is filtered off and washed with hot 3% ammonium nitrate containing some of the precipitation mixture (5 ml of the latter to 100 ml of ammonium nitrate).

Filter paper plus precipitate are dried and ashed in a platinum or porcelain crucible; the residue – thorium dioxide – is finally calcined in an electric oven to constant weight.

Experiments have shown that one precipitation of thorium as the hydroxide is sufficient to separate this element from the rare earths; usually there is no need to resort to reprecipitation.

When very large amounts of the rare earths are present, the thorium isolated can be reprecipitated. When this has to be done, the filter paper plus thorium hydroxide are carefully ashed in a porcelain crucible; they are then calcined at a low temperature to burn off the carbon, the oxide obtained is dissolved in nitric acid sp. gr. 1.5, and precipitation repeated as described above. The method can also be used in preparative work.

SUMMARY

Thorium is quantitatively precipitated by means of a mixture of pyridine and its nitrate at a pH of 4.1-4.2. Ammonium nitrate accelerates coagulation and settling out of the precipitate. Thorium hydroxide is precipitated in a very dense form which exhibits a very low absorptive capacity. Yttrium, lanthanum, trivalent cerium, neodymium, praseodymium, erbium, samarium, and ytterbium remain in solution.

Thorium is precipitated in such a pure state that reprecipitation is not necessary.

LITERATURE CITED

[1] E.A. Ostroumov and S.A. Beruch'ian, Factory Labs. 12, 802 (1946).

[2] A. Jefferson, J. Am. Chem. Soc. 24, 540 (1902).

[3] J. Watters and J. Kolthoff, Ind. Eng. Chem., Anal. Ed. 16, 187 (1944).

[4] E.A. Ostroumov, New Methods for Chemical Analysis Using Organic Bases*(State Geol. Press, Moscow, 1952).

[5] H.T.S. Britton, Hydrogen Ions* *(ONTI, 1936).

[6] E.A. Ostroumov, Factory Labs. 13, 404 (1947).

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*In Russian.
**Russian translation.

A STUDY OF A PHOTOMETRIC METHOD OF DETERMINING CERIUM AS THE PEROXIDE COMPLEX

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For the photometric determination of cerium, of the greatest importance is the method based on the formation of a colored compound by the action of hydrogen peroxide in an alkaline medium [1-4]. This method permits determination of cerium in the presence of other rare earths. The latter are precipitated as a whole in the form of oxalates; the precipitate of the latter is then dissolved by some method or other, after which cerium is determined. Formation of a colored compound occurs in nitrate and alkali media [2, 5, 7], or in ammonia [6], as well as in a medium of a 50% solution of potassium carbonate [2, 5, 7].

The experiments we have carried out on the methods recommended confirmed the reproducibility and specificity of the formation of a colored compound. The reaction is also characterized by high sensitivity [3, 4]. On measuring the light absorption on an FEK-M photocolorimeter using a blue-light filter and a 2 cm cell, we found that the molar absorption coefficient Q_m is equal to approximately 800.

At the same time the methods described in the literature suffer from some serious disadvantages. The most important drawback is that the colored peroxide compound of cerium is insoluble in water. Plank [1], who was the first to suggest the methods under consideration, carried out determinations in a medium of concentrated potassium carbonate solution without using hydrogen peroxide, cerium being oxidized by atmospheric oxygen. Plank noted that addition of hydrogen peroxide gives a more rapid color effect, nevertheless, under such conditions a precipitate separates out. In more recent work [3, 4] the workers have not considered this point, and have not adopted any special measures for eliminating the effect of solid phase formation. Experiments have shown, however, that this last factor presents the greatest difficulty. Even when the recommended procedures are strictly adhered to, usually after a short time (0.5-3 minutes) a turbidity develops or a precipitate separates out. Comparison of colors in a colorimeter or in a photocolorimeter often becomes completely impossible.

Experiments have shown that formation of the colored peroxide compound of cerium is strongly dependent on the acidity of the solution. It is practically impossible to find a favorable alkalinity range. In acid medium, and also at a pH of 7 or 8, the color is attenuated or does not appear at all, while at pH 8 or 9 and above, coagulation or turbidity of the solution is observed.

Riabchikov and Strelkova [3] recommend that for each test solution one should take a series of samples and experimentally choose the amount of 0.1 N NaOH, in which (in the presence of H_2O_2) the colored compound is formed, but in which no precipitate separates out. Using this technique we succeeded in preparing solutions for measurement of the optical density of the colored complex. Nevertheless, in the course of ordinary analysis, solutions are obtained which differ in their initial acidity and, accordingly, a lot of time and test solutions are used up in establishing the amount of alkali necessary for each separate solution. Attempts which we made to simplify this technique, for example by controlling the pH by means of indicator papers, did not yield positive results.

The Use of Glycerol for Stabilizing Cerium Peroxide Suspensions

The first problem was to find a method for preparing sufficiently stable solutions of the colored peroxide

complex of cerium. For this purpose we tested various media. Thus, we studied the action of a series of water immiscible organic solvents for extracting the complex. We were, however, unable to find such a solvent; it was observed that many, in particular isoamyl alcohol, readily float the peroxide complex of cerium. Next, various materials which give soluble complex compounds with hydrogen peroxide (urotropine, urea, etc) were tested. These materials, however, showed no observable effect. Various stabilizers were tested with the intention of keeping the colored complex in a state of suspension. It was found that gelatine, starch, gum-arabic, and a number of other materials exhibit no appreciable stabilizing effect. It was found, however, that glycerol is a good stabilizing agent. Citrate solutions in which a turbidity develops, on following the procedures usually recommended, were clear and suitable for photometric measurements when about 20% by volume of glycerol was added beforehand. Experiments showed that glycerol only acts as a stabilizing agent in the presence of a complexing agent. Addition of gylcerol alone (e.g., without citrate or a complexon) does not give a transparent colored solution.

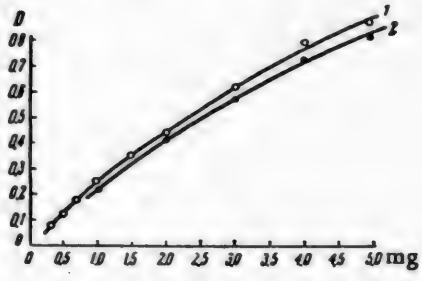
Tests also showed that increasing the amount of citrate increases the stability of the colloidal suspension somewhat. At the same time, a large amount of citrate complexes part of the cerium. and prevents formation of the colored peroxide compound, thereby leading to a decrease in optical density. The solutions used in these measurements were prepared as follows. To 1 ml lots of an almost neutral solution containing 5 mg of cerium as the nitrate, were added various amounts of a saturated solution of sodium citrate, these were followed in succession by 1 ml of 0.1 N NaOH, 0.25 ml of 10% H_2O_2, and the volumes made up to 50 ml with water. Optical density was measured on an FEK-M apparatus using a blue filter and a 3 cm cell. The results of one such series is given below.

Number of milliliters of saturated citrate solution	2	5	10	20
Optical density	0.79	0.59	0.33	0.028

Thus, on increasing the citrate concentration, the optical density drops considerably (2-20 times).

In the literature [3, 5] it is recommended that the oxalate precipitates of the rare earths be treated on the filter with a saturated solution of sodium citrate until the oxalates dissolve completely. The results just given show that during this process it is necessary, at least, to fix the amount of citrate in the test and standard solutions accurately.

We obtained satisfactory results on using glycerol. Experiments were carried out according to the following procedure. The original solution used was one of $Ce(NO_3)_3$ acidified slightly with nitric acid and containing 5 mg of cerium per ml. 0.1 to 1 ml lots of this solution corresponding to cerium contents ranging from 0.5-5 mg were chosen for photometric measurements. The cerium solution was transferred to a 50-ml standard flask, to which was then added two drops of a saturated solution of sodium or potassium citrate, 1 ml of 0.1 N NaOH, 20 ml of glycerol (1 : 1), and five drops of 10% hydrogen peroxide solution. Formation of the colored compound requires five to eight minutes. Water was then added to bring the volume up to the mark, and the solution allowed to stand for a few minutes to let oxygen bubbles escape. Measurements were carried out as indicated above. The results obtained are shown on the diagram, Curve 2.



Relation between optical density (D) and the cerium content in mg: 1) in the presence of Complexon III and glycerol; 2) in the presence of citrate and glycerol.

Solutions not containing glycerol were prepared for comparison. In these cases, the optimum amount of 0.1 N NaOH was established beforehand in each case. The following procedure was adopted in order to do this. Known amounts of cerium were introduced into a series of 50-ml standard flasks; 1, 2, 3, etc. drops of 0.1 N alkali was then added and the procedure given in [3] then followed. A scale was thereby obtained in which the color intensity increased right up to the appear-

ance of turbidity. In order to construct a curve, the value of the optical density corresponding to a cerium solution which had the maximum color, but in which turbidity had not yet appeared, was taken. Since, as already mentioned above, such a method of preparing solutions is not convenient for analysis, we only used this method for studying the effect of various factors. Results of optical density measurements were approximately 8% higher than those obtained when glycerol was used. Thus, glycerol depresses the sensitivity of the method slightly. Nevertheless, the stability of the colored solution with time increases considerably, and preparation of such solutions does not take long. The use of glycerol has the added advantage that the color intensity is independent of the volume of solution before addition of the H_2O_2. When glycerol was not used, it was observed that during the photometric determinations, the color weakened when the solution of the cerium salt was diluted before addition of H_2O_2.

Choice of Complexing Agent and the pH of the Medium

Comparison of various complexing agents showed that ethylenediamine tetracetic acid is the most convenient to use. When the reaction is carried out under those conditions normally recommended, the colored compound coagulates in 0.5-5 minutes. In the presence of Complexon III there is formed a colored cerium complex which is characterized by a high degree of dispersion, so that even in the absence of glycerol, there is formed a suspension which is stable over a period of several hours. In the presence of glycerol and Complexon III, the colloidal suspension is stable for an even longer time.

It was pointed out above that the colored cerium complex is very sensitive to the pH of the medium. Even when glycerol was used, it was observed that insufficient ammonia strongly restrains color development, while a large excess of ammonia leads to opalescence. When insufficient alkali is present, the color, in addition, gets stronger with time. In order to avoid these phenomena, it is expedient to use a buffer solution with a pH of 9 (20 g ammonium chloride and 100 ml of concentrated ammonia were diluted to 1 liter).

The use of Complexon III and a buffer solution permits one, in the ordinary course of analysis, to do without glycerol. Buffer solution in amounts ranging from 1 to 10 ml on 50 ml of total volume has no effect on the value of the optical density. Nevertheless, increasing the amount of Complexon leads to a decrease in optical density; this is similar to the phenomenon described above in the case of the citrate. Thus, for a cerium content of 1 mg in 50 ml, the optical density in the presence of 2, 5, and 10 ml of 0.1 N Complexon III is 0.248, 0.232, and 0.201 respectively. The presence of a large amount of salts in solution weakens the color and decreases the stability of the colored suspension. In these cases it is best to use glycerol.

On the basis of the facts given above, we have developed the following procedure for the photometric determination of cerium. To solutions containing from 0.5-5 mg of cerium in the form of its citrate or chloride, are added 2 ml of 0.1 N Complexon III solution, 10 ml of glycerol (1 : 1), and the solution neutralized with ammonia until it has a faint smell of the latter (or until litmus paper turns blue); 5 ml of buffer solution and five drops of 10% hydrogen peroxide are then added. After five minutes the volume is made up to the mark with water, the whole thoroughly mixed and, after 20-30 minutes, colorimetric measurements carried out using a blue filter and a 2 cm cell; water is used as reference. The results obtained are shown on the diagram, Curve 1.

Dissolving Rare Earth Oxalates

Usually cerium is determined on the precipitate of rare earth oxalates taken as a whole. It is often recommended that these oxalates be brought into solution by calcining them to form the oxides, and then dissolving the latter in acids. It is known, however, that calcined cerium is difficult to dissolve in acids. Some procedures recommend that the oxalates be dissolved in excess complexing agent (citrate). Nevertheless, the latter, as shown above, complicates formation of the colored cerium compound. In this connection therefore we attempted to dissolve the rare-earth oxalates by means of acid with addition of persulfate or permanganate for oxidizing the oxalate ions.* For this purpose the precipitated oxalates were washed off the filter paper with water containing sulfuric or nitric acid, persulfate or permanganate was then added and the solution boiled. Excess of persulfate was destroyed by boiling, while excess permanganate was destroyed by addition of a few drops of hydrogen peroxide.

*The oxalates can also be converted into soluble chlorides by evaporating calcium and rare-earth oxalates a few times with aqua regia.

Of the two oxidizing agents tested, permanganate proved to be the best. Hydroxylamine can be used to keep manganese in solution during precipitation of rare-earth hydroxides by means of ammonia (for separating them from calcium).

The photometric method described has been used for many determinations of cerium in solutions of its pure salts and in synthetic mixtures containing aluminum and iron salts, after precipitation of cerium as the oxalate both with and without calcium, the oxalates being broken up by ashing and by oxidation with persulfate or permanganate. Cerium which ha been added to natural samples containing the rare earths was determined in the same way.

Work with synthetic mixtures showed that the error in the photometric determination of cerium in pure solutions of its salts is about ±5% (relative), which is not in excess of normal errors obtained during photometric determinations. After precipitation of cerium as the oxalate (either with or without a collector), and also during the analysis of mixtures containing 1-5 mg of cerium (as the nitrate) and 100 mg of iron or aluminum (as alum), after all the separation operations involved as described in the procedure, the deviation was slightly greater than ±6% relative; the maximum deviation was up to 20% relative. Under these conditions, the number of negative errors increase, this being determined by losses in cerium during the separation operations. Thus, of 26 experiments, only nine gave a positive error.

Cerium was subsequently determined by the procedure given below in natural materials containing 0.06-0.3% of cerium dioxide. During this series, cerium was added artificially to some of the samples. Comparison of the results of analysis on samples with and without addition of cerium indicated analogous results.

Photometric determination was carried out by the following technique. 1 g of test material was broken down with a mixture of hydrofluoric and sulfuric acids. The dry residue was treated with HCl (1:1) and the mixture heated; it was then transferred to a beaker and allowed to stand overnight. The insoluble residue was filtered off; when this residue had a dark color, it was given a second treatment with hydrofluoric and sulfuric acids, or fused with sodium carbonate, the dry residue was again dissolved in HCl (1:1), the solution filtered and the filtrate combined with the first filtrate.

The combined filtrates were evaporated and the hydroxides precipitated by means of ammonia. When aluminum was present, precipitation was carried out with the aid of sodium hydroxide in order to remove the aluminum from the rare earths. The precipitate was filtered and, without washing in situ, was washed into a beaker, 2-4 ml of a 5% solution of calcium chloride was added to the solution, followed by an equal volume of a solution of oxalic acid saturated with respect to the latter in the cold; the mixture obtained was heated almost to the boiling point. Using "universal indicator," ammonia was added until a pH of 3 was attained; the solution was then left to stand overnight. The oxalates were reprecipitated, since at high iron and aluminum contents, the oxalate precipitates trap part of these elements.

The rare-earth oxalates together with the collector – calcium oxalate – were filtered off and washed four to five times with a 1% oxalic acid solution; the precipitates were then carefully ashed at 500-600°, or dissolved in acid containing permanganate, as indicated above. The rare-earth hydroxides were separated from calcium by means of ammonia. The precipitate of hydroxides was dissolved in HCl on the filter. The hydrochloric acid solution was then used for photometric determinations, the latter being carried out as described above.

SUMMARY

A study has been made of the requisite conditions for the photometric determination of cerium as the peroxide complex. The main difficulty of the methods formerly advocated has been precipitation of the colored cerium compound. It is now suggested that the solution be stabilized by means of glycerol in the presence of Complexon III. When the latter is used, a highly dispersed form of the colored cerium complex is obtained and there is no need for a stabilizer.

It has been shown that it is possible to bring rare-earth oxalates into solution without calcining them; the alternative method suggested here is to dissolve the oxalates directly in sulfuric acid to which persulfate has been added, or in nitric acid containing permanganate.

LITERATURE CITED

[1] J. Plank, Z. anal. Chem. 116, 312 (1939).

[2] E.B. Sandell, Colorimetric Determination of Traces of Metals* (Goskhimizdat, 1949).

[3] D.I. Riabchikov and Z.P. Strelkova, J. Anal. Chem. 3, 226 (1948).

[4] N.S. Poluetkov and M.P. Nikonova, J. Anal. Chem. 3, 354 (1948).

[5] A.A. Tikhonova, Factory Labs. 19, 779 (1953).

[6] R.S. Volodarskaia, Factory Labs. 19, 1158 (1953).

[7] A.K. Babko and A.I. Volkova, Ukrainian Chem. J. 20, 211 (1954).

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PHOTOMETRIC DETERMINATION OF CERIUM AS CERIUMMOLYBDIC HETEROPOLY ACID

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Of the published methods for the photometric determination of small amounts of cerium, the most sensitive and widely used method is that based on formation of a colored complex with hydrogen peroxide in the presence of nitrates [1, 2], or carbonates [3, 4]; the persulfate [5], and the persulfate-brucine methods [6, 7], with benzidene [8, 9], gallic acid [10], alcohols [11], and veratrol [12], are all either of low sensitivity or are difficult to carry out. The essential drawback of the method involving hydrogen peroxide is the necessity for a preliminary separation of cerium from the heavy metals and molybdenum. Accordingly, we tried to develop a new method for the photometric determination of cerium which is based on the formation of the ceriummolybdic heteropoly acid.

First of all, experiments were carried out to try and establish the optimum conditions for the formation of the ceriummolybdic heteropoly acid.

1. Effect of molybdate concentration. Complete formation of the ceriummolybdate complex depends on excess molybdate in solution. The effect of sodium molybdate concentration at a hydrogen ion concentration equivalent to 0.2 N on completeness of formation of the ceriummolybdate complex was studied. To 1 ml of $Ce(SO_4)_2$ solution containing 0.20 mg of Ce, was added 0.54 ml of sulfuric acid (sp.gr. 1.115) to give a sulfuric acid concentration in the final solution of 0.2 N, and various amounts of a solution of sodium molybdate with a pH of 7. The solutions were diluted to 10 ml with water and the optical density of the solutions determined on a FEK-52 photocolorimeter at 360 mμ. The results of these measurements are given on Figure 1. In order to establish the optimum conditions for formation of ceriummolybdic acid, experiments were carried out on the effect of excess reagent (sodium molybdate), at various hydrogen-ion concentrations, on completeness of formation of the complex.

For this purpose, various amounts of sulfuric acid (sp.gr. 1.115) were added to 1 ml of $Ce(SO_4)_2$ solution containing 0.20 mg cerium, followed by a 60, 80, and 100-fold excess of sodium molybdate previously neutralized to a pH of 7. The volume was made up to 20 ml in each case. A solution of sodium molybdate with the same acidity was used as the reference solution. Measurements were made on a SF-4 spectrophotometer.

The results of these measurements are shown in Figure 2. As is evident from Figure 2, the optimum excess of sodium molybdate is a 60-fold excess.

2. Effect of hydrogen ion concentration. In order to find the optimum acid concentration for the formation of the ceriummolybdate complex, various amounts of sulfuric acid, and 5 ml of a 5% solution of sodium molybdate (60-fold excess) were added to a solution of $Ce(SO_4)_2$ containing 1 mg, and the volume of the solutions made up to 10 ml with water; the optical density of the solutions obtained was then measured on a FEK-52 photocolorimeter at 360 mμ.

Water was used as the reference solution. The results obtained are shown in Figure 3.

The color intensity of solutions of the ceriummolybdate complex is considerably higher than that of $Ce(SO_4)_2$ solutions of the same concentration in 0.2-0.6 N H_2SO_4 (Figure 3).

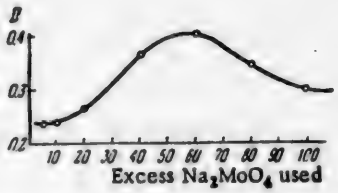

Fig. 1. Effect of sodium molybdate concentration, for a constant hydrogen ion concentration of $H^+ = 0.2$ N, on completeness of formation of cerium molybdate complex.

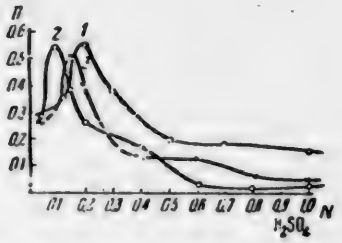

Fig. 2. Effect of excess sodium molybdate, for various hydrogen ion concentrations, on completeness of formation of the cerium-molybdate complex: 1) 60-fold excess of molybdate; 2) 80-fold excess of molybdate; 3) 100-fold excess of molybdate.

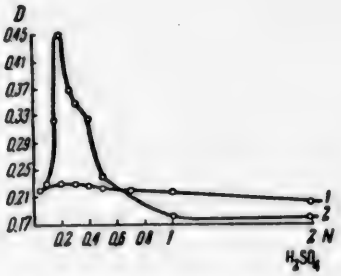

Fig. 3. Relation between the color intensity of cerium sulfate solutions (1), and of cerium molybdate heteropoly acid solutions (2) and the acidity, for a 60-fold excess of molybdate.

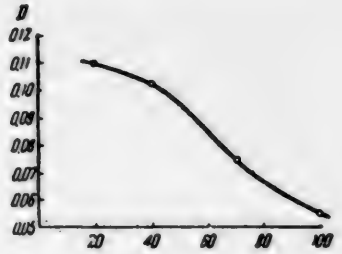

Fig. 4. Relation between the color intensity of the cerium molybdate heteropoly acid formed and temperature.

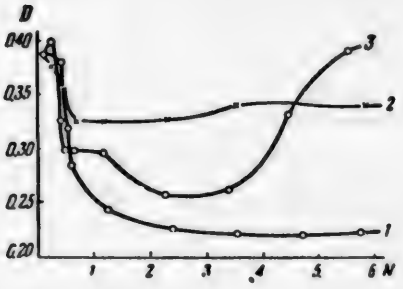

Fig. 5. Change in color intensity of the cerium molybdate complex formed with changes in hydrogen ion concentration in mineral acids: 1) nitric; 2) sulfuric; 3) hydrochloric.

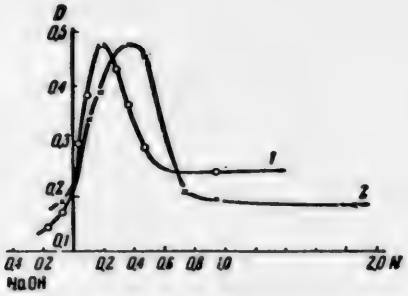

Fig. 6. Stability of the cerium molybdic heteropoly acid in the presence of sulfuric (1) and perchloric (2) acid.

As Figure 3 shows, the optimum hydrogen ion concentration for the formation of the cerium molybdic acid is 0.2 N with respect to H_2SO_4.

A Study of the Stability of the Ceriummolybdic Heteropoly Acid

Ceriummolybdic acid, as the results given in the table show, is fairly stable with time.

All the same, the stability of the ceriummolybdate complex changes with changes in temperature (Figure 4). The stability of the ceriummolybdate complex formed with changes in hydrogen ion concentration of the solution was studied as follows.

TABLE

Relation Between Color Intensity of Ceriummolybdic Heteropoly Acid and Time

Time	0	5 min	10 min	15 min	20 min	30 min	40 min	50 min	1 hour	1 hour 15 min	1 hour 25 min
D	0.432	0.430	0.429	0.430	0.432	0.428	0.420	0.419	0.415	0.400	0.400

To a solution of ceriummolybdic acid prepared in 10 ml of 0.2 N H_2SO_4 (0.54 ml H_2SO_4, sp.gr. 1.115, 1 ml of $Ce(SO_4)_2$ containing 0.20 mg cerium, 5 ml of 5% neutral sodium molybdate solution, made up to 10 ml with water), ten minutes after formation of the heteropoly acid, was added water and mineral acid in order to give various acidities. The total volume was 20 ml. The optical density of the solutions was measured on a FEK-52 photocolorimeter at 360 mμ. Water was used as the reference solution. The results of these measurements are shown in Figure 5. As is evident from Figure 5, ceriummolybdic acid breaks down on increasing the hydrogen ion concentration. The special shape of the curve relating the optical density of the solution to increasing hydrochloric acid concentration is determined, obviously, by a side oxidation-reduction reaction. A comparative study of the behavior of the ceriummolybdate complex in media made from sulfuric and perchloric acid showed that the ceriummolybdate complex breaks down with increasing hydrogen ion concentration, and not as a result of the complexing of cerium into a sulfate complex. These results are shown in Fig. 6.

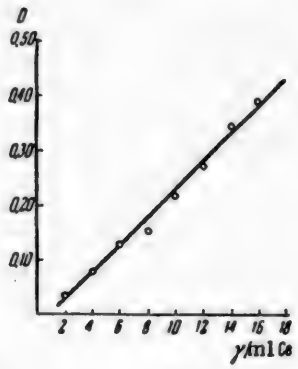

Fig. 7. Calibration curve for determination of 0.025-0.4 mg Ce.

Experiments showed that the ceriummolybdate complex is stable over a narrow hydrogen ion concentration range, namely in media of 0.1-0.3 N H_2SO_4 and in a medium 0.4 N with respect to perchloric acid. Nevertheless, the comparatively narrow hydrogen ion concentration range does not prevent one from using formation of the ceriummolybdate complex for the photometric determination of cerium.

The color intensity of solutions of ceriummolybdic acid conform to Beer's law. A calibration curve for determination of 1-16 γ of Ce/ml in 0.2 N H_2SO_4 is shown in Figure 7. The sensitivity of the reaction is 1 γ Ce/ml.

Cerium can be determined photometrically as follows: to a solution containing 0.025-0.4 mg of cerium is added sulfuric acid until the concentration of the latter in the final volume is 0.2 N, 12 ml of a 5% neutral solution of sodium molybdate is then added (or 10 ml of a 5% solution of ammonium molybdate), and the solution diluted with water to 25 ml; after ten minutes the optical density is measured on a SF-4 spectrophotometer at 380 mμ (slit width 0.4 mm).

SUMMARY

A new method has been developed for the photometric determination of cerium, which is based on the formation of ceriummolybdic heteropoly acid. The conditions of formation and the stability of the ceriummolybdate complex have been studied.

LITERATURE CITED

[1] D.I. Riabchikov and Z.G. Strelkova, J. Anal. Chem. 3, 226 (1948).

[2] A.K. Babko and A.I. Volkova, Ukrainian Chem. J. 20, 211 (1954).

[3] R.J. Meyer, Z. anorg. Chem. 41, 97 (1904).

[4] E. Plank, Z. anal. Chem. 116, 312 (1939).

[5] E.B. Sandell, Colorimetric Determination of Traces of Metals* (1949), pp. 508-511.

[6] F.M. Shemiakin, V.A. Volkova and A.S. Bozhko, J. Gen. Chem. 8, 452 (1938).

[7] F.M. Shemiakin and V.A. Volkova, J. Gen. Chem. 9, 698 (1939).

[8] T.K.S. Murphy and B.S.V. Rao, J. Indian. Chem. Soc. 27, 383 (1950).

[9] E. Herzfeld, Z. anal. Chem. 115, 421 (1939).

[10] F.M. Shemiakin, Factory Labs. 3, 1090 (1934).

[11] A. Fouchet, Chim. anal. 36, 234 (1954).

[12] H.N. Antonides, Chemist-Analyst 44, 2, 34 (1955); Referat Zhur. Khim. 58408 (1956).

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ANALYTICAL APPLICATION OF PHENOLCARBOXYLIC ACIDS OF THE TRIPHENYLMETHANE SERIES

DETERMINATION OF VANADIUM IN STEELS BY MEANS OF ALUMINON

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In a previous article [1] it was shown that the qualitative reaction for vanadium ions using aluminon, a reaction which had been suggested by V.I. Kuznetsov [2, 3], can be used for the photometric determination of vanadium in pure solutions. The conditions for carrying out this reaction were also described in that article in detail: the relations between the optical density of the solution and the analytical form of test material, pH, temperature, and time were established; the composition of the complex was determined; and the accuracy and reproducibility of the method were established.

TABLE 1

pH Limits for the Interaction of Aluminon With Various Cations (Acetate and acetate-ammoniacal [5] buffer solutions)

Cation, C-1000 γ/ml	Interaction pH range	Color of the reagent at the limits of the pH range		Color of the analytical form
		acid	alkali	
Mo^{VI}	1-4	Rose*	Rose	Raspberry
Cr^{3+}	2-5.5	Rose*	Pale-rose	Red*
Th^{IV}	2-7	Rose*	Colorless	Rose*
Sn^{2+}	2-7	Rose*	Colorless	Rose*
VO^{2+}	2-7	Rose*	Colorless	Raspberry
UO_2^{2+}	2-7	Rose*	Colorless	Raspberry
Al^{3+}	2-9	Rose*	Colorless	Raspberry*
Fe^{3+}	2-9	Rose*	Colorless	Violet*
Ce^{III}	2-9	Rose*	Colorless	Red*
Tl^{IV}	2-11	Rose*	Colorless	Red*
Cu^{2+}	4-9	Rose	Colorless	Raspberry*
Be^{2+}	4-9	Rose	Colorless	Red
Pb^{2+}	6-9	Pale-rose	Colorless	Rose*
Co^{2+}	7-9	Colorless	Colorless	Rose*
Zn^{2+}	7-9	Colorless	Colorless	Rose*
Mn^{2+}	7-9	Colorless	Colorless	Rose*
Cd^{2+}	7-11	Colorless	Colorless	Rose*
Ni^{2+}	9-11	Colorless	Colorless	Rose*
Mg^{2+}	9-11	Colorless	Colorless	Rose*
Ca^{2+}	11 and higher		Colorless	Rose

*A colored precipitate separates out.

The interaction of the vanadyl ion with aluminon is of considerable analytical importance: it is characterized by a fairly high sensitivity, and occurs rapidly; reaction takes place over a wide concentration range, within which the solution of the reaction product conforms to the Lambert-Beer law; the reagent is fairly readily obtainable.

TABLE 2

Quantitative Determination of VO^{2+} in the Presence of Other Elements

V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV} : Me	V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV} : Me
	Ni^{2+}					Ca			
5	5000	5	0	1 : 1000	5	2000	5	0	1 : 400
30	5000	33	−3		100	2000	100	0	
5	10000	5	0	1 : 2000	5	10000	8	+3	1 : 2000
30	10000	30	0		30	10000	31	+1	
90	10000	85	−5		80	10000	90	+10	
	Co^{2+}					Zn^{2+}			
5	5000	5	0	1 : 1000	5	2000	7	+2	1 : 400
70	5000	68	−2		100	2000	100	0	
5	10000	8	+3	1 : 2000	5	5000	7	+2	1 : 1000
60	10000	60	0		30	5000	31	+1	
					100	5000	80	−20	
	Mn^{2+}	5	0	1 : 2000		Cd^{2+}			
5	5000	33	+3		5	1000	6	+1	1 : 200
30	5000	5	0	1 : 2000	80	1000	80	0	
5	10000	62	−8		5	3000	5	0	1 : 500
70	10000				60	3000	75	−15	
	Mg^{2+}					Mo^{VI}			
5	5000	5	0	1 : 1000	5	100	5	0	1 : 20
20	5000	20	0		50	100	52	+2	
100	5000	90	−10		100	100	100	0	
5	10000	7	+ 2	1 : 2000	5	200	8	+3	1 : 40
50	10000	41	− 9		100	200	95	−2	

We studied this reaction further in detail with the aim of using it for the determination of small amounts of vanadium in steels.

Aluminon is not a specific reagent for the vanadyl ion. The specificity of the reaction can be increased by controlling the hydrogen ion concentration. Many organic reagents generally react with various elements only at certain pH values [4]. The pH limits for the reaction of aluminon with various ions are given in Table 1.

It is evident from this table that many ions interact with aluminon at pH values which differ from those for the vanadyl ion. Thus, the alkali and alkaline-earth metals, as well as Mn^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, As^{V}, W^{VI}, Hg_2^{2+}, Hg^{2+} do not interfere with the reaction for the vanadyl ion.

The limiting ratios for a number of cations, in the presence of which vanadium can be determined quantitatively by means of aluminon, are given in Table 2.

The results given in Table 2 show that relatively large amounts of such ions as Co^{2+}, Ni^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+} and Cd^{2+} do not interfere with vanadium determination.

All the same, Al^{3+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, Be^{2+}, Th^{IV}, Ce^{III}, Ti^{IV}, and UO_2^{2+} form colored compounds with the reagent, in the pH range which is most favorable for vanadium determination. The results given in Table 3 show that some ions are as sensitive to aluminon as the vanadyl ion.

All the facts adduced above indicate that in developing a method for the determination of vanadium in steels by means of aluminon, it is essential to take into account the specificity of the reagent, and to eliminate interference on the part of some of the elements which usually accompany vanadium.

There are fairly reliable methods available for removing interference from iron the main component of steel; one of these is reduction with ascorbic acid [6]. As for chromium, which is also a steel component, we

are unaware of any simple, reliable, and convenient methods for removing this metal from vanadium; usually, they are separated from each other by electrolysis on a mercury cathode [7], by a chromatographic method [8], or by choosing reagents, where chromium does not affect the results of vanadium determination considerably [9].

TABLE 3

Sensitivity of the Reaction Between Aluminon and the Ions of Certain Elements

Cation	VO^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}	Be^{2+}	Mo^{VI}	Tl^{IV}	Ni^{2+}	Co^{2+}	Th^{IV}	UO_2^{2+}	Cu^{2+}	Mg^{2+}	Ca^{2+}
Sensitivity in γ/ml	0.1	0.05	0.5	25	0.25	25	1.25	0.5	50	2	2.5	0.5	0.5	10
Optimum pH	4	4	3.22	4	4	2.8	4	9	7	4	4	5	11	11

In order to prevent interference by iron and chromium we used thioglycollic acid; this reagent forms a pale-green colored complex with trivalent chromium [10, 11]; on heating in an acetate buffer with a pH of 3.4-3.8, this color becomes appreciably paler.

Table 4 contains results for the determination of vanadium by means of aluminon in the presence of iron and chromium, after addition of thioglycollic acid.

Thus, by adding thioglycollic acid, interference from practically any amount of iron can be eliminated. Chromium, which gives a colored complex with thioglycollic acid, does not interfere with vanadium determination up to a limiting ratio of 1:200.

TABLE 4

Determination of Vanadium in the Presence of Iron and Chromium After Masking With Thioglycollic Acid

V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV}:Me	V^{IV} taken, in γ	Me added, in γ	V^{IV} found, in γ	Error, in γ	Ratio V^{IV}:Me
	Fe^{3+}					Cr^{3+}			
5	500	5	0	1:100	5	500	4	−1	1:100
25	500	23	−2		40	500	38	−2	
5	1000	7	+2	1:200	90	500	90	0	
60	1000	61	+1		5	1000	5	0	1:200
5	10000	6	+1	1:2000	30	1000	31	+1	
50	10000	49	−1		50	1000	50	0	
100	10000	98	−2		70	1000	67	−3	

In order to prevent interference by iron and chromium, a known amount of a 2.5% solution of thioglycollic acid should be added. The order in which the reagents are added is also of essential importance: a known amount of thioglycollic acid is first added to the test solution, the buffer solution is added next, and, finally, the aluminon solution. In order that the thioglycollic acid does not change the pH of the solution, it is neutralized beforehand with alkali (to Congo Red).

Determination of Vanadium in Steels

0.8-1.0 g* of steel is dissolved in 40-50 ml of HCl (1:1) in a porcelain dish covered with a watch glass,

*For vanadium contents less than 0.5%.

by heating on a water bath. The watch glass is removed and the contents of the dish evaporated until the volume is 10-15 ml, 1-2 ml of concentrated HNO_3 is then added and the solution evaporated to dryness. 5-10 ml of HCl (1:1) is added to the residue and the whole evaporated to dryness once again.* The residue is moistened two to three times with a small amount of water (15-20 ml), and the solution evaporated to 5 ml, 2-3 ml of a 20% solution of hydroxylamine and 10-15 ml of water are then added. The solution is boiled for 15-20 minutes and then transferred to a 100-ml standard flask. After cooling, the solution is diluted to the mark with water and thoroughly mixed; from an aliquot of this solution the silica is filtered off (through a dry funnel into a dry flask). For determination of the vanadium, 1 ml of this filtered solution is transferred to a 10-ml beaker and 0.15-0.25 ml of a 2.5% solution of thioglycollic acid added, the latter having been neutralized to the Congo Red end point beforehand; the solution obtained is then warmed slightly on a water bath for one to two minutes, it is cooled and 5 ml of buffer solution with a pH of 3.72-3.86 added, followed by 0.3 ml of gum arabic (2%), and the final solution again heated on a water bath for five minutes. To the cooled solution is finally added 0.5 ml of a 0.25% solution of aluminon; the liquid in the beaker should then have a volume of 6 ml.

TABLE 5

Determination of Vanadium in Steels

Steel sample	Specified vanadium content	Vanadium content as determined by the method developed above	Difference, in %
30-a	0.26	0.27	+0.01
		0.26	0
		0.26	0
		0.25	−0.01
30-b	0.24	0.235	−0.005
		0.24	0
		0.22	−0.02
		0.24	−0
124	0.24	0.23	−0.01
		0.24	0
		0.24	0
No. 1	0.09	0.108	+0.018
		0.09	0

The aluminon solution used was prepared by dissolving the dye on heating for 10-15 minutes on a water bath at 80-90°.

Five minutes after addition of the aluminon the optical density is measured, using a green filter (λ about 530 mμ). The vanadium content is found by means of a calibration curve constructed under the same conditions as those used for the test sample.

The method described above has been widely checked on various types of steel (Table 5) during student practice on the analysis of ferrous and nonferrous metals at Saratov University.

SUMMARY

A photocolorimetric method has been developed for the determination of vanadium in steels of certain grades, without having to resort to preliminary separation of interfering ions.

*This procedure for getting the sample into solution probably ensures complete breakdown of the vanadium carbides contained in the test steel samples, since the results obtained were in complete agreement with the specified contents.

LITERATURE CITED

[1] E.A. Kashkovskaia and I.S. Mustafin, Part I, Sci. Proc. Saratov State University (in the press).

[2] V.I. Kuznetsov, Proc. Acad. Sci. USSR 50, 39 (1946).

[3] V.I. Kuznetsov and L.S. Kozyreva, J. Anal.Chem. 8, 90 (1953).•

[4] V.I. Kuznetsov, J. Gen. Chem. 22, 816 (1950).•

[5] A.K. Babko, Physicochemical Analysis of Complex Compounds in Solution•• (Izd. AN Ukrainian SSR, 1955), p. 97.

[6] I.M. Korenman,J. Appl. Chem. 13, 309 (1940).

[7] S.I. Frid, Factory Labs 11, 17 (1945).

[8] I. Kraus, Detection and Colorimetric Determination of Vanadium After its Chromatographic Separation from Accompanying Elements•• Author's Thesis (Leningrad, 1955).

[9] Iu.M. Morachevskii and M.N. Gordeeva, Bull. Leningrad University 11, 139 (1955).

[10] F. Welcher, Organic Analytical Reagents IV, 1948, 159.

[11] I.V. Dubsky and V. Sindelar, Mikrochim. Acta 3, 258 (1938).

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A COLOR REACTION FOR URANIUM WITH THE REAGENT ARSENAZO

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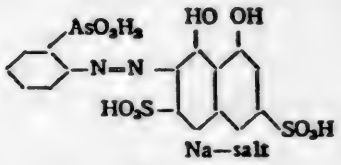
Ions of U^{IV} and U^{VI} form chromophoric atomic groupings; Muller [1] as long ago as 1920 turned his attention to this point. As a consequence of this, color reactions are possible for uranium which are based on its chromophoric action [2]. A number of color reactions for uranium, or more accurately uranyl, described in the literature, belong to this category. All reactions which are based on the use of noncolored reagents belong to this category; they include salicylic [3], sulfosalicylic [4, 5], aminosalicylic [6], gallic [7], resorcylic [7], or para-cresotic [8] acids, tannin [7], pyrocatechol disulfonic acid [9], aminopyrocatechol [6], dibenzoylmethane [10, 11], oxalohydroxamic acid [12], dihydroxyacetophenoneoxime [13], furoacetyl-2,5-diethoxyaniline [14], salicylamide [15], thiocyanates [16-18], sodium diethyldithiocarbamate [19], and many others. To this category belong, in addition, the carefully studied reaction with H_2O_2 [20], which has been recommended for the photometric determination of uranium [21, 22], and the reaction with $K_4Fe(CN)_6$ [23-25]. Photometric methods of determination which are based on the chromophoric effect have also been described for quadrivalent uranium [26].

Color reactions which are based on the chromophoric effect of elements are of relatively low sensitivity, for reasons which have been considered in detail elsewhere [27]. Color reactions with colored organic reagents are more sensitive. In such reactions, the color changes are related to changes in the ionic state of the colored reagents [28]. Since the inherent color of the reagents themselves is very intense, color reactions of this type are very sensitive. A number of such color reactions for uranium have been described in the literature; they include reactions with: quinalizarin [29], alizarin S [30], curcumin [31], quercetin and quercetrin [32], anthrazo [33], 4-amino-4-hydroxy-3'-carboxyazobenzene-2-sulfonic acid [6], 4-amino-3',4'-dihydroxyazobenzene-2-sulfonic acid [6], 4-amino-2-arsonic acid <1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid [6], etc.



Arsenazo
(Uranon I)

To this latter group of reagents belongs the reagent arsenazo which has been described previously ("Uranon I"; benzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid); this reagent gives highly sensitive, and very contrasting color reactions, with both sexivalent [34], and quadrivalent [35] uranium. Arsenazo has also been recommended for color reactions with, and for the photometric determination of the rare earths [36], zirconium [37], thorium [34, 35, 38], aluminum [39], beryllium [40], and quadrivalent vanadium [41].

The present article contains a description of a color reaction for uranium (U^{VI} and U^{IV}) with arsenazo.•

•The reaction was developed by the author in 1944.

The quantitative photometric determination of uranium by means of this reagent will be described later. A description of the synthesis of the reagent has been described previously [36].

Arsenazo (the sodium salt) is a dark brown crystalline powder which is readily soluble in water to give solutions of a red-rose color. The color does not change on acidification but changes to raspberry when its solution is made alkaline. Strong oxidizing agents (elemental chlorine and bromine, permanganate, hypochlorite) and reducing agents (Sn^{II}, Ti^{III}, $Na_2S_2O_4$) decolorize and break down the reagent. H_2O_2 does not affect the reagent in the cold.

Arsenazo gives color reactions – violet colors of different shades – with a number of elements [36, 40]. The effect of pH on the development of the color reactions of different elements is found to be in complete agreement with the general rules: the more readily does a given ion hydrolyze, the lower the pH of the solution in which arsenazo gives a color reaction [42, 43]. In accordance with this rule, U^{IV} like Th, gives a color reaction (blue-violet color) in a mineral acid medium, while U^{VI} (blue or light blue), like the rare earths and Be, only gives a color in a very weak acid medium, at pH 4.5-5.5.

Although arsenazo gives color reactions with many other elements apart from uranium, by carrying out the reaction under certain conditions, uranium can be detected quite reliably. A check reaction with H_2O_2 guarantees correct results even when deviations are made from the procedure that should be followed.

Detection of sexivalent uranium in pure solutions and in the presence of elements which do not react with arsenazo (K, Na, NH_4, Ca, Sr, Ba, Mg, Mn) is carried out as follows: to 1 ml of weakly acid or neutral test solution is added one drop of 3 N HCl and one to two drops of 0.02-0.05% aqueous arsenazo solution. A rose color indicates the absence of Th, U^{IV}, Zr, Ti, and Fe^{III}; three to four drops of a 25% solution of urotropine is then added. When U^{VI} is present a pure blue or violet color appears; when excess reagent is added, the color immediately changes to the original rose color of the reagent after addition of a drop of H_2O_2. The limit of identification is 0.2γ of U^{VI}; the limiting dilution is $1:5\cdot10^6$.

The blue color which develops in the presence of insufficient reagent is characteristic of sexivalent uranium alone and is suitable for providing convincing proof of its presence, since none of the other elements give a blue or pale blue color. Violet colors of different shades may develop in the presence of Th, U^{IV}, TR, V^{IV}, Al, Fe^{III}, Zr, Ti, Cu, Be, Cr, Ga, and Pd as well, but these colors (apart from those of U^{IV} and V^{IV}), after addition of H_2O_2, do not change immediately. The colors developed in the presence of U^{IV} and V^{IV} disappear immediately on addition of H_2O_2; nevertheless, these elements, even in the presence of insufficient reagent, only form violet colors and not the blue color formed by U^{VI}.

Fluorides, phosphates, arsenates, vanadates and H_2O_2, when present in amounts which are five to ten times that of the uranium present (in terms of U, F, P, As, V) and large amounts of sulfates, suppress the reaction considerably. Complexon III, salicylates, and sulfosalicylates exhibit only a weak effect.

When the reaction is carried out as a spot test, it is best to use filter paper which has been soaked with a 0.2% aqueous solution of arsenazo and dried. It is useful to have a capillary with a very fine diameter of about 0.2 mm at its tip.

A drop of the weakly acid test solution is evaporated on the lid of a crucible, and the residue dissolved in a micro drop of urotropine (ten drops of 25% urotropine + two drops of 3 N HCl) and the solution obtained taken up in the capillary. By touching the reagent filter paper with the tip of the capillary, some of the test solution is expressed.

When uranium is present a blue spot develops; this disappears on moistening with dilute H_2O_2.

The limit of identification is 0.05γ of U in a micro drop of 0.005 ml at a dilution of $1:1\cdot10^5$.

Detection of quadrivalent uranium in the presence of rare earths, V^V, Th, V^{IV}, Al, Fe^{II}, Be, and other elements is carried out as follows. By addition of HCl or CH_3COONa, an acidity of 0.02-0.05 N is created in the test solution; this is assessed by comparison with the color of methyl violet paper,* which has been moistened with 0.02 and 0.05 N HCl. To 1 ml of a solution prepared in this way is added a drop of 0.01-0.05% arsenazo solution. The development of a violet color which slowly changes to a rose color on addition of a drop of H_2O_2

*This can be prepared by soaking filter paper with a dilute solution of the usual "chemical" (violet) ink.

indicates the presence of U^{IV}.

The limit of identification is 1-2 γ of U^{IV}.

Detection of U^{IV} is possible in the presence of a thousand times its amount of U^{VI}, V^{IV}, the rare earths and Be, and in the presence of Al and the divalent cations (Fe^{II}, Cu, Mn, Mg, etc.). In the presence of Fe^{II} the check reaction with H_2O_2 is of little use. Th, Zr, Ti, Fe^{III}, give colors which do not change immediately on addition of H_2O_2. Those anions which complicate detection of U^{VI} interfere, as well as tungstates and molybdates.

Detection of uranium (U^{VI}) in the presence of elements which react with arsenazo. By using selective masking, uranium can be detected in individual cases even in the presence of elements which react with arsenazo. The rare earths interact with arsenazo after complexing of any uranium which is present. Accordingly, since the colors formed by U^{VI} and the rare earths differ, on addition of arsenazo in small portions to a solution containing urotropine, it is possible to detect uranium in the presence of the rare earths at ratios of U^{VI}: rare earths = 1:1000. Comparison with a control test containing the rare earths alone is necessary.

Trivalent iron can be converted into Fe^{II} by the action of $Na_2S_2O_3$, ascorbic acid, or other reducing agents; uranium can then be detected at ratios of U^{VI}: Fe = 1:300 and higher. Urotropine should be added after addition of $Na_2S_2O_3$. Under the experimental conditions used, a large amount of Fe^{II} can lead to decomposition of the reagent.

Fluorides complex aluminum to a greater extent than U^{VI}. By adding fluoride in an amount which is only sufficient to mask aluminum, uranium can be detected in the presence of the latter. The test solution which has been treated with urotropine, and which weakly colors arsenazo, is split up into two separate beakers. To one is added a few drops of H_2O_2 and then to both beakers is added dropwise, at the same time and in equal amounts, a saturated solution of Na_2SiF_6 or a 0.5% NaF solution; the latter is inferior to Na_2SiF_6.

When no uranium is present, the color in both beakers changes to the same extent, the change being a gradual one from violet to rose. When uranium is present, the color of the solution to which H_2O_2 has not been added becomes more and more blue, becoming a pure blue if not too much aluminum is present, while the contents of the beaker containing the solution to which H_2O_2 has been added almost acquires the color of the reagent.

Detection of uranium is still possible at a ratio of U: Al = 1:250. When the amount of aluminum is twenty times that of uranium, a blue color can still be observed. In the presence of only three to four times its amount of aluminum, uranium can be detected directly.

Thorium and zirconium in amounts not more than ten times that of the U^{VI} can be masked by means of fluorides in the same way as aluminum. Copper can be masked by addition of $Na_2S_2O_3$.

Beryllium is complexed by addition of salicylates. 0.1 ml of a 10% solution of ammonium salicylate complexes 160 γ Be, thereby permitting detection of 20 γ of U in solution; this corresponds to a ratio of U: Be = = 1:8.

For the detection of sexivalent uranium in the presence of interfering phosphates or arsenates, the latter can be conveniently separated by means of stannic acid whereby, at the same time, the readily hydrolyzable ions Zr, Ti, Th, U^{IV}, Fe^{III}, Nb, and Ta can be removed. Such a separation is readily carried out by using "stannic chloride" (an approximately 60% aqueous solution of $SnCl_4$). On addition of a few drops of this "stannic chloride" to 0.02-0.03 N hydrochloric acid test solution, with subsequent heating, metastannic acid separates out and the latter traps the phosphates and arsenates and the elements whose cations hydrolyze readily. When the acidity is not less than that indicated, uranium (U^{VI}) remains quantitatively in solution together with aluminum, the rare earths, beryllium, and all the elements whose cations hydrolyze with difficulty. Work should be carried out in very dilute solutions. For facilitating coagulation of the stannic acid, particularly in the presence of iron, whose hydroxide forms a stable colloidal system with the hydrosol of metastannic acid [44], it is useful to add 3-5% NH_4NO_3. When separation with metastannic acid has been carried out successfully, the acid filtrate does not give a color reaction with arsenazo and does not become turbid on addition of urotropine.

Detection of uranium in minerals and rocks. When the uranium content is high – of the order of several percent – uranium can be detected, in several instances, without its preliminary separation from other elements. For the study of uranium minerals, a small particle of rock which is hardly visible is sufficient.

A few milligrams of the mineral which has been finely ground to a powder is heated in a test tube with two to three drops of a mixture of HCl and HNO_3 (3:1)*; 5 ml of water is added, and a very small piece of Congo Red paper placed in the solution; a drop of a saturated solution of $Na_2S_2O_3$ is then added. When the violet color (from Fe^{III} and $Na_2S_2O_3$) has disappeared, a 25% solution of urotropine is added dropwise until the Congo Red paper has turned red; two to three drops of urotropine are then added in excess. A 0.01-0.05% solution of arsenazo is next added to the solution. When uranium is present, a blue color appears, which slowly changes to a rose color on addition of H_2O_2. When iron is present, a brown precipitate of ferric hydroxide appears at this stage.

When the uranium content is low, 0.5-1 g of finely ground material is heated in a test tube with 1-2 ml of a mixture of HCl and HNO_3 (1:3). The solution is washed into a flask, and, without filtering, its volume is made up to about 100 ml, a piece of Congo Red paper is introduced into the flask, and $NaHCO_3$ solution added until the Congo paper is violet; 10-20 drops of the commercial aqueous 60% $SnCl_4$ solution is then added and the solution heated to the boil; after the precipitate has coagulated it is filtered off. Another piece of Congo paper is introduced into the filtrate, and 25% urotropine solution added until the indicator paper is red, 0.5 ml of urotropine solution is added in excess, arsenazo reagent is added and the solution divided into two. To one half is added a few drops of H_2O_2, after which a saturated solution of Na_2SiF_6 or a 0.5% solution of NaF is added to both halves dropwise, in equal amounts, and at the same time with thorough agitation.

When uranium is present, the contents of the beaker to which H_2O_2 has been added acquires an almost rose color, while the half to which no H_2O_2 has been added becomes violet.

Samples containing 0.005% uranium still give a clear-cut reaction for uranium, but with higher contents of aluminum, the reaction is not so distinct.

For detection of quadrivalent aluminum, 2-5 mg of finely ground mineral is placed in a very narrow test tube, and one drop (about 0.03 ml) of 6 N HCl is added; the mixture is carefully heated, care being taken to avoid evaporation of the drop. 2 ml of water is added and the solution heated to the boil for a further minute, it is then cooled and a drop of 0.01-0.05% solution of arsenazo added. The appearance of a violet color which changes immediately to rose on addition of a drop of H_2O_2 testifies to the presence of quadrivalent uranium.

SUMMARY

Arsenazo reagent (benzene-2-arsonic acid-<1-azo-7>-1,8-dihydroxynaphthalene-3,6-disulfonic acid) dissolves in water to give solutions of a red-rose color; the latter, in the presence of uranium, changes to blue (sexivalent, pH about 4.5-5.5) or violet (quadrivalent, mineral acid media). U^{VI} is detected by addition to the acid test solution of reagent and urotropine. The limiting dilution for uranium is $1:5\cdot10^6$. On addition of H_2O_2, the color immediately changes to rose (check reaction). By using NaF, $Na_2S_2O_3$, and salicylates for masking, it is possible to detect U^{VI} in the presence of the rare earths, Fe, Al, Th, Zr, Cu and Be. Quadrivalent uranium in mineral acid media can be detected directly in the presence of large amounts of U^{VI}, the rare earths, V^{IV}, Be, Al, Fe^{III}, Cu, Mg, and a number of other elements. Cations (Fe^{III}, Zr, Ti, Th) and anions (phosphates, arsenates) which interfere with the reaction can be removed by coprecipitation with metastannic acid, which separates out during hydrolysis of added $SnCl_4$ solution. Qualitative reactions for U^{VI} and U^{IV} are described, together with procedures for detecting U^{VI} and U^{IV} in minerals.

LITERATURE CITED

[1] A. Müller, Z. anorg. Chem. 109, 235 (1920); J. prakt. Chem. (N.F.) 157, 89 (1940).

[2] V.I. Kuznetsov, Progr. Chem. 21, 175 (1952).

[3] A. Müller, Chem. Z. 43, 739 (1919).

[4] M.C. Darnell and B.S. Walker, Ind. Eng. Chem. Anal. Ed. 12, 242 (1940).

[5] R.T. Foley and R.C. Anderson, J. Am. Chem. Soc. 71, 909 (1949).

*Silicates are fused in the loop of a platinum wire with soda, the melt is then treated, and acidified, and the procedure outlined for acid decomposition subsequently followed.

[6] V.I. Kuznetsov, Proc. Acad. Sci. USSR 50, 233 (1945).

[7] P.N. Das-Gupta, J. Ind. Chem. Soc. 6, 763 (1929).

[8] B.R. Repman, Laboratory Practice 1, 27 (1941).

[9] J.H. Yoe and A.R. Armstrong, Anal. Chem. 19, 100 (1947).

[10] J.H. Yoe, F. Will and R.A. Black, Anal. Chem. 25, 1200 (1953).

[11] R. Pribil and M. Jelinek, Chem. Listy 47, 1326 (1953).

[12] A.K. Das-Gupta and J. Gupta, Chem. Abs. 45, 5059 (1951).

[13] H.K. Urs and K. Neelakantam, J. Sci. Ind. Research (India) 11B, 79 (1952).

[14] W.E. Clark and L.R. Stallings,Chem. Abs. 36, 3114 (1942).

[15] A.K. Chakraburtty, D. Sen and B. Ray, J. Ind. Chem. Soc. 30, 491 (1953).

[16] J.E. Currah and F.E. Beamish, Anal. Chem. 19, 609 (1947).

[17] M. Gerhold and F. Hecht, Mikrochemie 36/37, 1100 (1951).

[18] C.E. Crouthamel and C.E. Johnson, Anal. Chem. 24, 1780 (1952).

[19] R.J. Lacoste, M.H. Earing and S.E. Wiberley, Anal. Chem. 23, 871 (1951).

[20] J. Corpel, Referat Zhur. Khim. 1954, 21496, No. 7.

[21] O. Hackl, Z. anal. Chem. 119, 32 (1940).

[22] T.R. Scott, The Analyst 75, 100 (1950).

[23] F. Feigl and R. Stern, Z. anal. Chem. 60, 39 (1921).

[24] N.A. Tananaeff and G.A. Pantschenko, Z. anorg. Chem. 150, 164 (1926).

[25] M. Kohn, Chem. Analyst 35, 52 (1946).

[26] R.G. Canning and P. Dixon, Anal. Chem. 27, 877 (1955).

[27] V.I. Kuznetsov, Collection, Trans. Conference on Spectrophotometric and Colorimetric Methods of Analysis,* XII (Moscow, 1955), pp. 15-17; Trans. Commission on Anal. Chem. VIII(IX), 52 (1957).*

[28] V.I. Kuznetsov, J. Anal. Chem. 6, 193 (1951).

[29] A.N. Majumdar, Chem. Abs. 42, 6701 (1948).

[30] F.G. Germuth, Am. J. Pharm. 101, 46 (1929).

[31] C. Zimmermann, Lieb. Ann. 204, 224 (1880).

[32] E.A. Kocsis, Mikrochemie 25, 13 (1938).

[33] V.I. Kuznetsov, J. Anal. Chem. 1, 259 (1946); J. Appl. Chem. 13, 769 (1940).

[34] V.I. Kuznetsov, Proc. Acad. Sci. USSR 31, 895 (1951); Author's Certificate 61967 (1942).

[35] V.I. Kuznetsov, Proc. Acad. Sci. USSR 50, 229 (1945).

[36] V.I. Kuznetsov, J. Anal. Chem. 7, 226 (1952).**

[37] V.I. Kuznetsov, L.M. Budanova and T.V. Matrosova, Factory Labs. 22, 406 (1956).

[38] M. Ishibashi and S. Higashi, Japan Analyst 4 (1), 14 (1955); Anal. Abstr. 2, 2387, No. 9 (1955).

[39] V.I. Kuznetsov and R.B. Golubtsova, Factory Labs. 21, 1422 (1955); 22, 161 (1956).

*In Russian.

**Original Russian pagination. See C.B. translation.

[40] V.I. Kuznetsov, J. Anal. Chem. 10, 276 (1955).*

[41] V.I. Kuznetsov, Proc. Acad. Sci. USSR 52, 39 (1946).

[42] V.I. Kuznetsov, J. Anal. Chem. 2, 67 (1947).

[43] L.M. Kul'berg, Organic Reagents in Analytical Chemistry** (Goskhimizdat, Moscow, 1950).

[44] C. Leperz and L. Storch, Monats. 10, 283 (1889).

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POLAROGRAPHIC DETERMINATION ON SOLID ELECTRODES OF OZONE AND CHLORINE IN THE AIR OF INDUSTRIAL CONCERNS

COMMUNICATION II*

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Determination of Ozone in Air

The limiting permissible ozone concentration of the air, according to Lazarev and Astrakhatsev's results [1], is 0.0001 mg/liter. Of the chemical methods for determining ozone in air, worthy of mention are those based on oxidation of $NaNO_2$ [2], and of potassium iodide with subsequent titrimetric determination of the iodine liberated.

An electrochemical method [3] based on the polarographic determination of iodine liberated during the interaction of ozone with potassium iodide has been developed. The luminescence method of determining ozone in air [4] is not applicable when other oxidizing agents are present in the air.

The problem confronting us was to develop a method which would permit determination of small concentrations of ozone in small volumes of air, using the solid rotating electrode technique. Solid electrodes have been used in polarography by a number of workers [5-9]. The basis of the method was oxidation of potassium iodide with ozone according to the following equation:

$$O_3 + 2I^- + H_2O \rightarrow I_2 + O_2 + 2OH^-. \quad (1)$$

The amount of iodide ions remaining after oxidation was determined polarographically on a rotating solid anode, in a supporting electrolyte of 0.1 N chloride or hydrochloric acid.

The anode was a smooth platinum wire 1 mm in diameter and 17 mm long twisted into a spiral. The cathode was a large calomel electrode. Contact was realized through an agar bridge. A synchronous motor rotated the electrode at the rate of 750 rpm.

In a supporting electrolyte of 0.1 N HCl, at molar concentrations of potassium iodide ranging from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ moles/liter, the strength of the diffusion current is proportional to the concentration of the iodide ions.

The half-wave potential for potassium iodide is equal to +0.55 volt (with respect to the saturated calomel electrode). Oxidation of potassium iodide on a platinum anode gives normal polarographic waves with clearly defined limiting currents (Figure 1). Complete reproducibility of the current strength and the polarograms is observed. The straight line calibration curve is shown in Figure 1.

Quantitative Determination of Ozone in Air

Ozone was prepared in a gas chamber with a capacity of 0.9 m^3 by means of a PRK-2 ultraviolet lamp.

*Communication I, see J. Anal. Chem. 11, 313 (1956), (See C.B. Translation.)

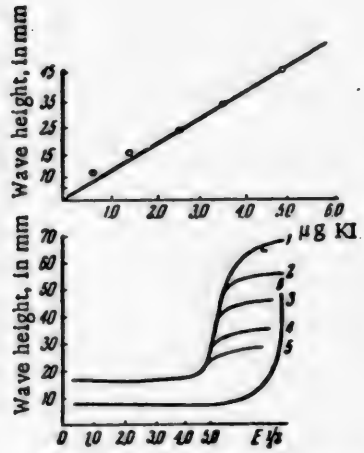

Fig. 1. Polarograms and calibration curve for potassium iodide in the concentration range 0.5-5γ KI: 1) 3.75γ; 2) 3γ; 3) 2.2γ; 4) 1.5γ; 5) 1.0γ; 6) 0.

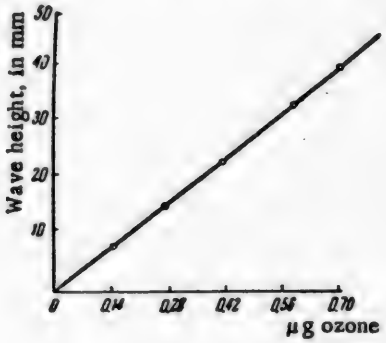

Fig. 2. Calibration curve for ozone.

TABLE 1

Results of Determinations of Ozone in Air as a Function of the Time of Standing of the Test Sample in the Bottle With Test Air

Time from moment of sampling to analysis, in minutes	Ozone found in 1 liter of air, in γ
30	0.29
60	0.33
90	0.26
180	0.27
240	0.33
300	0.27
380	0.23

Air samples were taken from the chamber into 5-liter darkened bottles, from which the air had been pumped out [10]. Before samples were taken, an absorption solution containing 10 γ of KI was introduced into the bottles. The sampled ozonized air was left for 1-1.5 hours in the dark. The walls of the bottle were moistened with the absorption solution. For analysis, a measured amount of the absorption solution from the bottle was transferred to a porcelain basin. The solution was evaporated to dryness on a water bath. The residue was dissolved in the basin in 0.5 ml water. The basin was rinsed with 1 ml of 0.1 N HCl, and the solution transferred to the electrolyzer and polarograms taken.

At the same time, a solution of KI containing 10γ KI was introduced into another basin; this solution was evaporated to dryness and the residue dissolved in 0.5 ml water; 1 ml of 0.1 N HCl was finally added, and the polarograms taken again.

The wave heights found in the two polarograms for sample and the KI solution, respectively, were subtracted from each other.

The amount of ozone in the sample was then established by means of the calibration curve (Figure 2).

The calibration curve for ozone was derived from the curve drawn for potassium iodide, after appropriate conversion of the amount of potassium iodide to ozone by means of Equation (1).

Blanks were carried out at the same time as the quantitative determination of the ozone in the air of the chamber. For this purpose, before the ultraviolet lamp was switched on, a ventilator was introduced into the chamber and, after ventilation of the chamber, a sample of air was introduced into an evacuated bottle. The analysis was carried out as described above.

Thirty minutes (Table 1) was found to be sufficient for the reaction between the ozone and the solution of potassium iodide in the bottle to go to completion at ozone concentrations of 0.2-0.3 γ/liter.

Table 2 contains the results for determination of ozone in the air of the chamber.

It was found that under the experimental conditions used, nitrogen dioxide does not interfere with determination of ozone in air; nitric acid was detected in amounts of 4.2-5.7 γ/liter in the air. We are of the opinion that the nitrogen dioxide is oxidized by ozone into nitric acid.

The method described for the determination of ozone in air has been used for developing health precautions in industrial establishments [11].

Determination of Chlorine on Solid Electrodes

The limiting permissible concentration of chlorine in air is 0.001 γ/ml.

Our problem was to develop a sensitive and accurate method – no less accurate than existing methods – requiring small volumes of test air of the order of 0.5-1 liter.

The basis of our method of determining chlorine was oxi-

TABLE 2

Determination of Ozone in the Air of the Chamber

Conditions under which sample was taken	Ozone found in 1 liter of air, in γ
10 minutes after PRK-2 lamp had been switched on, without ventilation	0.47
15 minutes after lamp was switched on	0.46
20 minutes " "	0.46
30 minutes " "	0.40
55 minutes " "	0.26

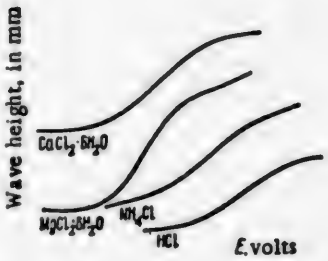

Fig. 3. Polarograms of KI solutions as a function of electrolyte composition.

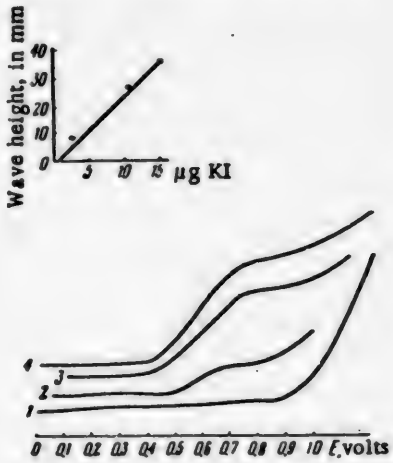

Fig. 4. Polarograms for iodine ions in a supporting electrolyte of 0.5 N $MgCl_2 \cdot 6H_2O$: 1) supporting electrolyte – 0.5 N $MgCl_2 \cdot 6H_2O$; 2) 3γ KI; 3) 10γ KI; 4) 15 γ KI.

dation of potassium iodide by chlorine according to the following reaction: $Cl_2 + 2I^- = I_2 + 2Cl^-$.

The potassium iodide remaining after the reaction was determined on a solid rotating electrode [12].

The effect of the supporting electrolyte on the diffusion current of KI is evident from Table 3.

Complex waves are observed in sulfuric acid media. In nitric acid media and also in sulfate and nitrate solutions, the waves for oxidation of iodine are poorly defined and cannot be used for the quantitative determination of KI.

The nature of the current-voltage curves are shown in Figure 3.

It is evident from the results obtained that chlorides can be used successfully as the supporting electrolyte for the quantitative determination of I^-. A 0.5 N solution of $MgCl_2 \cdot 6H_2O$ is preferred since the height of the diffusion wave for KI in this supporting electrolyte is higher than those obtained in other chlorides.

Polarograms for I^- in a supporting electrolyte of 0.5 N $MgCl_2 \cdot 6H_2O$ are shown in Figure 4, as well as the calibration curve for chlorine.

For the quantitative determination of chlorine by the polarographic method, chlorine water was prepared by saturation of twice distilled water with pure, gaseous chlorine. By appropriate dilution of the chlorine water thus prepared, solutions were prepared with chlorine concentrations of the order of $1.2 \cdot 10^{-4}$ M/liter. The chlorine concentration of the chlorine water was determined iodometrically before each test. For analysis, solution of chlorine water was added to a KI solution of known concentration. The solution was evaporated to dryness. The residue was dissolved in water, and the solution obtained transferred to an electrolyzer; polarograms were then taken in a supporting electrolyte of 0.5 M $MgCl_2 \cdot 6H_2O$.

At the same time polarograms were taken for a solution of KI taken in the same amount as that for analyzing the chlorine.

TABLE 3

Effect of the Supporting Electrolyte on the Diffusion Current of KI

Supporting electrolyte, 0.1 M solution	Wave height, in mm	KI concentration, in γ
KCl	14	10
$MgCl_2 \cdot 6H_2O$	27	10
NH_4Cl	23	10
$BaCl_2$	27	10
$CaCl_2$	20	10
HCl	20	10

TABLE 4

Polarographic Determination of Chlorine on a Solid Rotating Electrode

Chlorine taken, in γ	Chlorine found, in γ	Amount determined, in %	Chlorine taken, in γ	Chlorine found, in γ	Amount determined, in %
0.42	0.58	138	3.4	2.95	86
0.85	0.70	82	4.25	3.35	78
1.27	1.45	113	4.40	3.85	87
1.70	1.57	92	8.5	6.37	75
2.12	1.95	92	10.5	8.55	81
2.55	1.95	76	17.0	13.3	78

The chlorine concentration was determined from the differences in height for the KI solution before and after addition of chlorine.

We carried out determinations of chlorine over the wide range of concentrations which are met in industrial-sanitation practice.

If small concentrations of chlorine are to be determined, sampling could be carried out by taking the air in evacuated bottles.

SUMMARY

1. A quantitative method of determining ozone in air is described which is based on the polarographic determination on a solid platinum anode of iodide ions which have not reacted with the oxidizing agent. Determination is carried out in a supporting electrolyte of 0.1 M HCl.

2. A method is described for determination of chlorine in liquids and air, which is based on the same principle as that used for ozone determination. The most satisfactory supporting electrolyte for chlorine determination is a 0.1 M solution of $MgCl_2 \cdot 6H_2O$. 0.1 M HCl can also be used as the supporting electrolyte.

3. The sensitivity of the method for ozone is 0.1γ, while for chlorine it is 0.5γ in 1.5 ml of liquid.

LITERATURE CITED

[1] N.V. Lazarev, Poisonous Materials in Industry* Part II (Goskhimizdat, Leningrad, 1954), p. 33.

[2] G.A. Gorodetskii, J. Appl. Chem. 9, 353 (1936).

[3] G. Paut and E. Glukauf, Nature 147, 614 (1941).

*In Russian.

[4] M.A. Konstantinova-Shlezinger, Luminescence Analysis* (Izd. AN SSSR, 1948), p. 199.

[5] E.M. Skobets and N.I. Atamenenko, Factory Labs. 15, 1291 (1949).

[6] E.M. Skobets et al., Factory Labs. 14, 131 (1948).

[7] Iu.S. Lialikov, Factory Labs. 17, 909 (1951).

[8] S.K. Chirkov, Factory Labs. 14, 1300 (1948).

[9] I.B. Kogan, J. Anal. Chem. 11, 313 (1956).**

[10] V.G. Gurevich, Determination of Poisonous Materials in the Air of Industrial Concerns* (ONTI, 1937).

[11] I.A. Frukht, I.B. Kogan and A.S. Lagunov, Brief Notes on the Scientific Work of the Institute of Hygiene and Professional Diseases for 1953-1954* (Khar'kov, 1955).

[12] Iu.S. Lialikov and V.I. Karmazin, Factory Labs. 14, 138 (1948).

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NEW METHOD FOR THE QUANTITATIVE DETERMINATION OF NITROGEN AND HALOGENS AND ALSO FOR THE DETERMINATION OF NITROGEN, SULFUR AND HALOGENS ON ONE ALIQUOT OF ORGANIC MATERIAL

COMMUNICATION IV

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In previous communications [1, 2] we have indicated that on heating nitrogen-, sulfur- and halogen-containing organic materials with powdered magnesium metal to temperatures of 550-650°, magnesium nitride, sulfide and halides are formed respectively.

The present article contains a description of a technique which permits simultaneous determination of two and three elements on one aliquot of organic material; in addition, the possibility is demonstrated of simultaneously determining sulfur and nitrogen in various types of coal.

Instead of hydrogen, which we used earlier for driving the air from the reaction tube, diethyl ether can be used. This simplifies the method considerably.*

EXPERIMENTAL

Simultaneous Determination of Nitrogen and Halogens on One Aliquot of Organic Material

A sample of the test organic material (0.05-0.10 g) is placed in a glass test tube 10-15 cm long and 1-1.5 cm in diameter; it is mixed with a small amount of magnesium and powdered magnesium metal sprinkled over it, until the tube is approximately half full. 0.5-0.7 ml of ether is introduced by means of a pipet into the test tube, and the test tube then placed in a beaker containing distilled water at a temperature of 40-50°. The test tube is completely filled with powdered magnesium and a further 0.5-0.7 ml of ether introduced; the tube is finally sealed with a stopper fitted with a rubber tube for leading away gases. The free end of this tube is led under a cylinder filled with water. The test tube is fitted into an electric oven, or is heated with a gas burner (Communication 1). After heating, the cooled, partially deformed test tube and its contents are ground up in a porcelain mortar and transferred quantitatively into a distillation flask for distilling off the ammonia. The air is displaced from the flask with carbon dioxide and the reaction mass treated with 25-35 ml of 40% sulfuric acid until the magnesium has completely dissolved. The solution is made alkaline with 15-20 ml of 50% potassium hydroxide, and the ammonia distilled off. It is best to use 0.1 N potassium biiodate for absorbing the ammonia [3]. Nitrogen is thereby determined iodometrically. When the ammonia has been removed (about one-third of the contents of the flask is distilled), the absorption flask is disconnected, and 10 ml of 10% potassium iodide added to it; after standing for five minutes the iodine liberated is titrated with 0.1 N sodium thiosulfate.

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*Replacement of hydrogen by ether was tried out at the suggestion of A.P. Terent'ev, to whom we should like to express our thanks at this juncture.

TABLE 1

Expt. No.	Test material and its formula	Amt test material, in g	0.1 N $KH(IO_3)_2$ used, ml	% Nitrogen			0.1 N $AgNO_3$ used up, ml	% Halogen		
				calc.	found	difference		calc.	found	difference
1	Tribromoaniline $C_6H_4Br_3N$	0.0402	1.20	4.25	4.18	−0.07	3.65	72.68	72 55	−0.13
		0.0492	1.40	4.25	3.98	−0.27	4.48	72.68	72.74	+0.06
2	Chloroaniline C_6H_6NCl	0.0487	3.70	10.98	10.65	−0.33	3.78	27.78	27.52	−0.26
		0.1010	7.80	10.98	10.82	−0.16	7.85	27.78	27.55	−0.23
3	Quinine hydrochloride $C_{20}H_{24}N_2O_2HCl\cdot 2H_2O$	0.0507	2.60	7.06	7.18	+0.12	1.30	8.94	9.09	+0.15
		0.0896	4.40	7.06	6.87	−0.19	2.20	8.94	8.71	−0.22
4	Bromoisovalerylurea $C_{12}H_{11}O_2N_2Br$	0.0462	4.20	12.73	12.56	−0.17	2.07	35.86	35.78	−0.05
		0.1028	9.95	12.73	12.48	−0.25	4.60	35.86	35.81	−0.10
5	Piperine $C_{17}H_{19}O_3N$	0.0519	1.80	4.90	4.86	−0.05				
	Tetrachlorophthalic acid $C_8H_2O_4Cl\cdot 1/2\,H_2O$	0.0490					6.30	45.32	45.58	+0.26
	Total aliquot	0.1009								
6	Piperine $C_{17}H_{19}O_3N$	0.0498	1.82	4.90	5.00	+0.10				
	Tetrachlorophthalic acid $C_8H_2O_4Cl_4\cdot 1/2H_2O$	0 0488					6.25	45.32	45.49	+0.17
	Total aliquot	0.0986								
7	Nitroanisole $C_7H_7O_3N$	0.0257	1.63	9.15	8.88	−0.23				
	Dibromobenzene $C_6H_4Br_2$	0.0275					2.33	67.70	67.71	+0.01
	Total aliquot	0.0532								
8	Nitroanisole $C_7H_7NO_3$	0.0247	1.57	9.15	8.90	−0.25				
	Hexachloroethane C	0.0263					6.67	89.85	89.92	+0.07
	Total aliquot	0.0510								
9	Nitroanisole $C_7H_7NO_3$	0.0251	1.60	9.15	8.93	−0.22				
	Tribromophenol	0.0248					2.25	72.43	72.50	+0.07
	Total aliquot	0.0499								
10	Nitroanisole $C_7H_7NO_3$	0.0242	1.54	9.15	8.91	−0.24				
	Tetrachlorophthalic acid $C_8H_2O_4Cl_4\cdot 1/2H_2O$	0.0271					3.45	45.32	45.13	−0.19
	Total aliquot	0.0513								
11	Oxanilide $C_{14}H_{12}O_2N_2$	0.0249	2.10	11.66	11.81	+0.15				
	Tetrachlorophthalic acid $C_8O_4Cl_4\cdot 1/2\,H_2O$	0.0255					3.25	45.32	45.19	−0.13
	Total aliquot	0.0504								

Note: In experiments Nos. 5-11, synthetic mixtures of materials containing nitrogen and halogens were analyzed.

TABLE 2

Expt. No.	Test material and its formula	Amount test material (g)	0.1 N I_2 solution used up, in ml	% Sulfur			0.1 N $KH(IO_3)_2$ used up, in ml	% Nitrogen			0.1 N $AgNO_3$ used up, in ml	% Halogen		
				calc.	found	difference		calc.	found	difference		calc.	found	difference
1	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0246	1.90	12.61	12.38	−0.23								
	p-Bromonitrobenzene $C_6H_4BrNO_2$	0.0304					1.50	6.94	6.91	−0.03	1.50	39.55	39.43	−0.12
	Total aliquot	0.0550												
2	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0248	1.90	12.61	12.28	−0.33								
	p-Bromonitrobenzene $C_6H_4BrNO_2$	0.0384					1.84	6.94	6.71	−0.23	1.90	39.55	39.54	−0.01
	Total aliquot	0.0632												
3	Sulfosalicylic acid $C_7H_6SO_6 \cdot 2H_2O$	0.0262	2.04	12.61	12.48	−0.13								
	Chloroaniline C_6H_6NCl	0.0302					2.34	10.98	10.85	−0.13	2.35	27.78	27.59	−0.13
	Total aliquot	0.0564												
4	Sulfosalicylic acid $C_7H_5SO_6 \cdot 2H_2O$	0.0222	1.75	12.61	12.63	+0.02								
	Chloroaniline C_6H_6NCl	0.0284					2.20	10.98	10.85	−0.13	2.25	27.78	28.09	+0.31
	Total aliquot	0.0506												
5	Naphthionic acid $C_{10}H_9NSO_3 \cdot 1/2\ H_2O$	0.0304	2.00	13 81	13.71	−0.10	1.30	6.03	5.98	−0.05				
	Iodoform CHI_3	0.0300									2.28	96.69	96.45	−0.24
	Total aliquot	0.0604												
6	Sodium alizarin sulfonate $C_{12}H_7O_7SNa \cdot H_2O$	0.0263	1.56	9.37	9.51	+0.14								
	p-Bromonitrobenzene $C_6H_4BrNO_2$	0.0340					1.61	6.94	6.63	−0.31	1.67	39.55	39.26	−0.29
	Total aliquot	0.0603												
7	Bis-(1,1-dimethylpentene-3-OH-sulfide) $C_{14}H_{24}O_2S$	0.0243	1.95	12.60	12.84	+0.24								
	Tribromoaniline $C_6H_4Br_3N$	0.0293					0.90	4.12	4.30	+0.18	2.68	72.68	73.09	+0.32
	Total aliquot	0.0536												
8	Sodium alizarin sulfonate $C_{14}H_7O_7SNa \cdot H_2O$	0.0224	1.30	9.37	9.30	−0.07								
	Chloroaniline C_6H_6NCl	0.0305					2.34	10.98	10.74	−0.24	2.40	27.78	27.89	+0.11

Note: Synthetic mixtures of materials containing sulfur, nitrogen, and halogens were analyzed.

TABLE 3

Expt. No.	Designation of test coal	Amt coal taken (in g) (on dry material)	% C^f	% H^f	% W^{as}	% A^{as}	% V^f	0.1 N I_2 solution used up, in ml	% Sulfur found VTI*	% Sulfur found NKI**	% Sulfur difference	0.1 N $KH(IO_3)_2$ used up, in ml	% Nitrogen found VTI*	% Nitrogen found NKI**	% Nitrogen difference
1	Coal AN-9739	0.1007	90.6	3.8	1.11	13.73	8.48	0.96	1,39	1.53	+0.14	0.86	1.24	1.19	−0.05
		0.0924	90.6	3.8	1.11	13.73	8.48	0.965	1.39	1.65	+0.27	0.67	1.24	1.01	−0.29
2	Coal AN-10100	0.1057	89.8	3.6	1.03	9.31	—	2.55	4.01	3.89	−0.12	1.06	1.39	1.40	+0.01
		0.0590	89.8	3.6	1.03	9.31	—	1.49	4.01	4.05	+0.04	0.67	1.39	1.59	+0.20
3	Coal 9986	0.1030	88.5	4.4	0.77	16.06	—	1.59	2.34	2.47	+0.13	1.15	1 38	1 56	+0.18
		0.0786	88 5	4.4	0.77	16.06	—	1.10	2.34	2.24	−0.10	0.86	1.38	1.53	+0.12
4	Coal AN-10050	0.0695	89.8	3.9	1.05	18.67	—	1.01	2.28	2.33	+0.05	0.77	1 40	1.55	+0.15
		0.0831	89.8	3.9	1.05	18.67	—	1.10	2.28	2.12	−0.16	0.68	1.40	1.15	−0,25
5	Coal AN-114	0.0656	77	—	2.90	22.90	45.2	0.52	1.12	1.27	+0.15	0.63	1.56	1.34	−0,22
		0.0930	77	—	2.90	22.90	45.2	0.81	1.12	1.39	+0.27	0.92	1.56	1.38	−0,18
6	Coal AN-8	0.0763	77	3.6	6.76	17.85	3.08	0.28	0.31	0.51	+0.20	1.01	2,14	1.86	−0.28
		0.0779	77	3.6	6.76	17.85	3,08	0.28	0.31	0.57	+0.26	1.06	2,14	1.98	−0.25
7	Coal AN-117	0.1012	86.6	—	0.61	25.48	25.6	1.06	1.60	1.68	+0,08	1.16	1,70	1.61	+0.09
		0.1220	86.6	—	0.61	25.48	25,6	1.35	1.60	1.77	+0.17	1.30	1.70	1.50	−0.20
8	Coal AN-96	0.1093	83.4	5.4	1.04	28.66	32.52	1.80	2.53	2.64	+0.11	1,20	1,61	1.53	−0.09
		0.1019	83.4	5.4	1.04	28.66	32.52	1.49	2.53	2.34	−0.19	1.02	1.61	1.40	−0.21

*According to the results of VTI (The Dzerzhinskdi All-Union Heat Technical Institute).

**According to the results of NKI (The S.O. Makarov Nikolaev Shipbuilding Institute): C^f is the percentage carbon on the fuel; H^f is the percentage of hydrogen on the fuel; W^{as} is the percentage of water in the analytical sample; A^{ds} the percentage ash on the dry sample; V^f is the percentage of volatile material on the fuel.

To the residue in the flask used for distillation is added 40% sulfuric acid until the precipitate of $Mg(OH)_2$ has dissolved; the solution is filtered free from carbon and the pieces of glass from the test tube. The filter is carefully washed with distilled water and the wash liquors combined with the filtrate. The halogen content of the filtrate is then determined argentimetrically.

The results obtained are given in Table 1.

Simultaneous Determination of Nitrogen, Sulfur and Halogens on One Aliquot of Organic Test Material

A sample of the organic test material is placed in a glass test tube and powdered magnesium added; the air is expelled by means of ether; the test tube and its contents are heated to 550-650° over a period of 20-30 minutes (as described above). When heating is finished, the cooled test tube is ground up in a porcelain mortar, and the material transferred quantitatively into a distillation flask for driving off the hydrogen sulfide [2]. The air is expelled from the apparatus by means of carbon dioxide, and the reaction mass treated with 25-35 ml of 40% sulfuric acid until all the magnesium has dissolved; the hydrogen sulfide is driven off and the sulfur determined iodometrically (see above). The flask used for distillation and containing the residue left after removal of hydrogen sulfide is then connected to a receiver for absorbing ammonia; the receiver contains 20 ml of 0.1N potassium biiodate. The acid solution in the distillation flask is made alkaline with 15-20 ml of 50% potassium hydroxide and, having driven off the ammonia, the nitrogen content of the original sample is determined iodometrically. After the hydrogen sulfide and ammonia have been removed, the contents of the flask are acidified with 40% sulfuric acid until all the $Mg(OH)_2$ has dissolved. The solid residues are filtered off and the filter carefully washed with distilled water; halogens are then determined in the combined filtrate and wash liquors.

The results obtained by this method are given in Table 2.

Table 3 contains the results obtained during analysis of various samples of industrial coal.

The method is fairly reliable and simple, and does not require any complicated apparatus and expensive materials; it should therefore find wide application in various laboratories.

SUMMARY

Quantitative methods are described for the simultaneous determination of nitrogen and halogens, as well as of nitrogen, sulfur, and halogens on one aliquot of an organic test material, coal for example.

LITERATURE CITED

[1] P.N. Fedoseev and N.P. Ivashova, J. Anal. Chem. 7, 113 (1952)•; 11, 233 (1956).•

[2] P.N. Fedoseev and N.P. Ivashova, J. Anal. Chem. 7, 117 (1952)•; 11, 22 (1956).•

[3] L. Niederl, V. Niederl and M. Eitington, Mikrochem. 25, 143 (1938).

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DETERMINATION OF NORMAL HYDROCARBONS IN PARAFFINS BY THE ADSORPTION ANALYSIS METHOD

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Determination of the normal-hydrocarbon content of commercial paraffins and ceresins is of considerable interest from the point of view of the industrial utilization of these materials. Thus, with increasing normal-hydrocarbon concentration of the paraffin to be oxidized, the efficiency of the latter increases and the composition of the distilled fatty acid improves considerably [1].

The techniques in current use for the quantitative separation of normal- and iso-hydrocarbons have serious drawbacks. The reaction of paraffin hydrocarbons with fuming sulfuric acid can, even under the best conditions, only be regarded as semiquantitative and cannot be used for the quantitative separation of normal- from iso-hydrocarbons [2, 3]. The classical nitration method of Konovalov [4], while permitting characterization of primary, secondary and tertiary carbon atoms, cannot be regarded as a strictly quantitative method either [5]. The method of determining iso-paraffins in a mixture with normal-paraffins by means of antimony pentachloride [2, 6-8] only permits determination of total hydrocarbons with a tertiary carbon atom, since antimony pentachloride reacts, not only with iso-paraffins, but also with naphthenic hydrocarbons.

The urea method of determining normal hydrocarbons has been finding wider application in analytical chemistry in recent years. It is known [9] that iso-hydrocarbons with strongly branched chains, and also cycloparaffins do not give penetration compounds with urea, since the cross section of the molecules of these compounds is considerably greater than the internal diameter of the elementary lattice cell of urea which is equal to 5A. Two variants of the urea method have been published. Hessler and Meinhardt [10] treat a solution of paraffin in carbon tetrachloride with a saturated solution of urea in methanol. The crystalline interaction product is then decomposed with water. Formation of the penetration compound is a reversible reaction and the final equilibrium state depends on a number of variables: temperature, concentration of the dissolved materials, nature of the solvent, ratio of solvent and activator (methanol, water, and other urea solvents are used as activators). It is difficult to take into account all these variables, accordingly, Hessler and Meinhardt have fixed these variables, and emphasize that even small deviations from their recommended procedure will lead to considerable errors of determination. Further, one must also bear in mind that hydrocarbons with weakly branched chains also penetrate into the urea lattice, the penetration being easier, the longer the hydrocarbon chain. This observation of Schlenk [11] has been confirmed by very recent work [12]. In general, both factors – dissociation of the urea complex and trapping of iso-compounds by the carbamide lattice – act in opposition on the final analytical results, but the extent of the mutual compensation of errors is not amenable to calculation.

Later, Hessler and Meinhardt, pursuing the aim of shifting the equilibrium toward formation of the penetration complex, made their method much more complicated by using a six-fold precipitation of normal-hydrocarbons with carbamide [13]. This technique involves a considerable increase in the amount of reagents necessary (1.4 liters of CCl_4, 1.4 liters of methanol and 420 g of urea are required for the analysis of 10 g of paraffin), while the time taken for one analysis becomes very great.

In the second variant proposed by Rosenberg, Genekh and Nikitina [14], the solution of test hydrocarbons is treated with solid urea and activator is added. The effect of dissociation of the complex and trapping of iso-compounds are not discussed in their article. From an experimental point of view, this second variant is incom-

parably simpler than that described in [10, 13].

The present article is devoted to further development of the determination of normal hydrocarbons by means of urea. Essentially, the work reduces to establishing an experimental basis for the assumption that the interaction of normal hydrocarbons with urea is an adsorption process, and to the development of a technique for the quantitative determination of normal hydrocarbons, based on the analysis of the adsorption isotherm.

EXPERIMENTAL

The interaction products of hydrocarbons with urea are not classical chemical compounds [15], not only because their formation does not conform to whole number stoichiometric ratios [11], but also because their energies of formation do not correspond in magnitude to Van-der-Waals' interaction forces. Actually, formation of the interaction products is accompanied by evolution of about 1.6 kilo calories per atom of carbon [16]. The formation energy of these complexes is scarcely twice the value of the heat effect, since their formation is accompanied not only by an increase but, more probably by a decrease in entropy, i.e., by an increase in order as compared with the original state of the system. In accordance with some ideas about the nature of this process outlined in [16], we suggest that interaction of urea with hydrocarbons is an adsorption process.

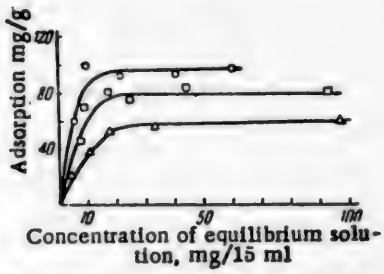

Fig. 1. Adsorption isotherms for hydrocarbon fractions: △) M = 338; □) M = 492; ○) M = 562.

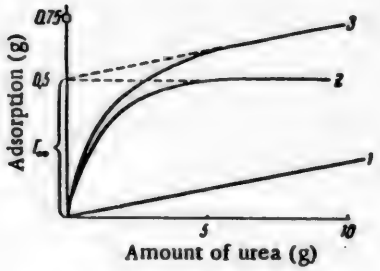

Fig. 2. Scheme for graphical extrapolation: 1) adsorption isotherm for iso-compounds; 2) adsorption isotherm for normal-hydrocarbons; 3) experimental isotherm; amount of paraffin in solution; amount of normal hydrocarbons in solution.

We have studied adsorption isotherms of narrow fractions of purified normal hydrocarbons on urea. The fractions were obtained by extractive crystallization from solutions of commercial paraffins and petroleum ether by means of urea. The molecular weight of the fractions was determined by measuring the dynamic viscosity at 55-80°. It is known that, at least for not too great temperature ranges, the viscosity is an exponential function of the absolute temperature [17, 18], i.e., the logarithm of the viscosity changes linearly with changes in the reciprocal of the absolute temperature:

$$\log \eta = \frac{B}{T} - A, \qquad (1)$$

where A and B are constants.

Mumford [19], having generalized the experimental results of many authors on the temperature relationship of the viscosity of liquid paraffin hydrocarbons, has shown that the constant B in Equation (1) is a linear function of the molecular weight.

From the slopes in Equation (1), and from the results given in [19], the mean molecular weights of the fractions were calculated.

Experiments on the study of the adsorption of these fractions were carried out at room temperature in 100 ml bottles with close fitting ground glass stoppers. The solvent used was benzene to which was added two percent by volume of methanol.* Chemically pure urea was ground up and sieved through a No. 25 sieve. 60 ml of solution and 1.2 g of urea were placed in each bottle. Shaking was carried out on a mechanical shaker for two hours. The paraffin concentration of the equilibrium solutions was determined by evaporating 10 ml of the solution. Some of the adsorption isotherms obtained are

*When activators are not added (alcohol, water) the paraffin fractions will not react with urea. It has been suggested [16] that the activators, which are urea solvents, form a pure adsorptive surface free from reaction inhibitors (sulfide and others). Preliminary tests showed that the solubility of urea in solutions containing 2% methanol lies outside the limits of the sensitivity of the experimental technique used in the work described in the present article.

shown in Figure 1.

The isotherms exhibit horizontal parts which correspond to limiting adsorption, and conform quite well to the Langmuir equation in the form

$$\frac{C}{\Gamma} = \frac{C}{\Gamma_\infty} + \frac{1}{k\Gamma_\infty}, \qquad (2)$$

where C is the equilibrium concentration, Γ is the adsorption in terms of grams per gram of urea, Γ_∞ is the limiting adsorption, and k is a constant.

From the results we obtained, it follows that the values of the adsorption coefficients, and also of the limiting values of the adsorption, are functions of the molecular weight of the fractions. Consequently, analysis of adsorption isotherms can be used as the basis of a quantitative method of determining normal hydrocarbons.

The problem forming the subject of the present article – total determination of normal-hydrocarbons in commercial paraffins – can be solved as follows. Adsorption isotherms are drawn by adding to a series of solutions containing the same amount of test paraffin, increasing amounts of urea. When the test paraffin contains only normal hydrocarbons the adsorption isotherm terminates in a clearly defined horizontal part, corresponding to complete adsorption of normal hydrocarbons. If, on the other hand, the test paraffin contains iso-hydrocarbons with weakly branched chains, the isotherm terminates (on addition of the same amount of urea) in a part which slopes to the abscissa and not in a horizontal part.

Actually, in the latter case the experimentally drawn adsorption isotherm is the resultant of two isotherms: the adsorption isotherm for normal-hydrocarbons and the adsorption isotherm for iso-hydrocarbons. Since the value of the adsorption coefficient of iso-hydrocarbons is very small, the adsorption isotherm of these hydrocarbons will be much lower than the isotherms for the normal-hydrocarbons, and the horizontal parts on them will be reached only after addition of very large amounts of urea. In other words, the horizontal parts of both isotherms are so far removed from one another along the abscissa, that over the range where the adsorption isotherm for normal-hydrocarbons is complete, the adsorption isotherm for iso-hydrocarbons can be depicted without serious error by a straight line. The isotherms for both processes and also the resultant (i.e., the experimental) isotherm, obtained by combining the ordinates of both isotherms, are schematically shown in Figure 2.

From Figure 2 it is evident that the normal-hydrocarbon content of the test paraffin fraction is equal to the intercept on the ordinate, obtained by extrapolating the sloping part of the resultant isotherm onto the ordinate corresponding to zero addition of urea.* The difference between the amount actually taken for analysis and the amount of normal hydrocarbons found by graphical extrapolation is equal to the isoparaffin content of the aliquot taken.**

This technique was used for the determination of normal hydrocarbons in four samples of commercial paraffins.

Analyses were carried out on solutions in benzene, toluene and carbon tetrachloride.*** In most cases, the adsorption isotherms of the commercial paraffins were compared with the isotherms of the same paraffins freed from isoparaffins. The adsorption isotherms obtained are shown in Figures 3-5. The final analytical results are given in the table, which also contains results obtained by other techniques (mainly by the Hessler-Meinhardt method).

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*This technique is completely analogous to the widely used method of dividing the over-all swelling process of high polymers into two stages: the swelling process proper, and the secondary stage which is determined by destructive oxidation of the polymer [20].

**By "isoparaffins" in contrast to the term "hydrocarbons of iso structure" we, in accordance with the tradition established in the literature on petroleum chemistry [21], mean those paraffin fractions which are not composed of hydrocarbons with normal structure. Hydrocarbons with a cyclic structure belong to this class of iso-hydrocarbons in addition to the iso compounds.

***Samples for analysis of solutions in carbon tetrachloride were taken by means of a pipet with a filter plug at the tip.

DISCUSSION OF RESULTS

Of interest is the difference in the paths followed by the adsorption isotherms of the original and the purified paraffins. In the latter, the isotherms terminate in clearly defined horizontal sections corresponding to almost complete adsorption of the dissolved paraffin, while the adsorption isotherm of the original paraffins is always lower than that for the purified paraffins, and terminates in straight line sections sloping toward the abscissa, which characterize the difficulty of adsorption of iso-hydrocarbons.*

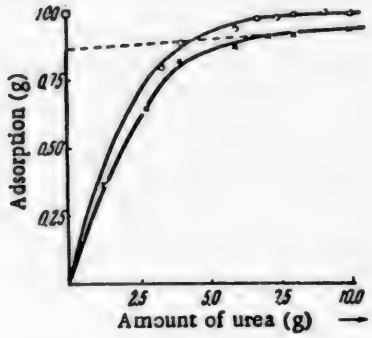

Fig. 3. Adsorption of paraffin No. 2 from benzene: O) purified paraffin; x) original paraffin; □) initial amount of paraffin in solution.

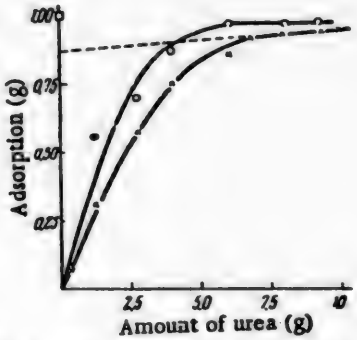

Fig. 4. Adsorption of paraffin No. 2 from toluene: x) original paraffin; O) purified paraffin; □) initial amount of paraffin in solution.

It is obvious from Figures 3-5 that the ordinates of the horizontal parts of the isotherms for the purified paraffins are approximately 1.5% less than the ordinates corresponding to the original aliquot. This difference is determined by errors in taking samples of solution for analysis and errors in converting the result of this analysis in terms of all the equilibrium solution on the one hand, and by errors which arise as a result of evaporation of solvent during shaking of the bottles (the stoppers, naturally, are not greased). The error which arises during graphical extrapolation of the sloping parts of the isotherms amounts to about 2%.

The content of normal hydrocarbons in the same sample of commercial material, as found by graphical extrapolation of the sloping section of the isotherm, is independent of the nature of the solvent. This conclusion is confirmed by the analytical results for paraffin No. 1 and particularly by those for No. 2, for which the adsorption isotherms were studied in three solvents: benzene, toluene, and carbon tetrachloride. These facts are convincing proof of the reliability of the technique suggested. The fact that the analytical results obtained for one sample in various solvents agree with one another, in most cases with an accuracy greater than 1.5%, is fully comprehensible since the sources of errors, mentioned above, are approximately the same for all solvents, and accordingly would be excluded.**

It is clear from the table that the results of analysis of paraffins studied during the course of the work described in the present article, and carried out by the Hessler-Meinhardt method, are close to those obtained by adsorption analysis but, in

*It is necessary to emphasize that Figure 2 is not connected with the curves shown on Figures 3-5. Actually, Figure 2 relates to a system of normal-paraffins + isoparaffins, while on Figures 3-5 a comparison is made of the isotherms of two systems: normal paraffins and commercial paraffins.

**It is of interest to quote the following example illustrating the efficiency of graphical extrapolation. Kolthoff and Kahn [22] have studied the adsorption of benzene solutions of butadienestyrene rubber on graphone. For one rubber the adsorption isotherm terminated in a horizontal section, while for the other it terminated in a sloping section; this behavior was attributed to the fact that in these rubbers, in addition to the sol fractions there is present a micro-gel fraction which is poorly adsorbed by the charcoal. In actual fact, it was found that the amount of rubber remaining in solution, according to the last point on the sloping section, was approximately equal to (but always slightly less than) the amount of the micro-gel fraction found by direct analytical methods. We extrapolated the sloping sections of the isotherms obtained by Kolthoff and Kahn to zero graphone content, and became convinced thereby that the amount of micro-gel in rubber calculated in this way, is almost in complete agreement with the analytically determined amounts.

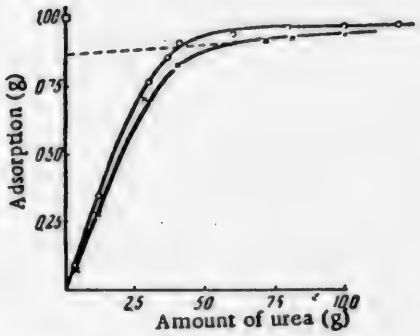

Fig. 5. Adsorption of paraffin No. 2 from CCl_4: x) original paraffin; O) purified paraffin; □) initial amount of paraffin in solution.

most cases, are somewhat lower. Even lower results were obtained when the Rosenberg, Genekh, Nikitina method was used. Presumably, for low contents of the iso-compounds, both sources of error suggested in [10, 14] as being characteristic of the analytical technique involving urea, namely dissociation of the complex and capture of the iso-compounds, compensate one another to a considerable extent. It is of interest to establish how complete such compensation would be in the case of analysis of compounds containing large amounts of iso-compounds, such as ceresines. We think that it is essential to emphasize that the techniques involving urea which have been suggested hitherto are equivalent to the study of one point on the adsorption isotherm of normal hydrocarbons by urea. Meanwhile, from the experimental results adduced in the present article, it follows that one well-defined conclusion regarding the content of normal hydrocarbons in paraffins can be made on the basis of the study of all the adsorption isotherms.

The method described is simple to carry out and permits work with small amounts of materials. We have obtained satisfactory results during work with 15 ml of solutions containing 0.25 g of paraffins. Since the method only demands analysis of equilibrium solutions, it is free from such operations as washing the complexes, their transfer from one piece of apparatus to another, decomposition of the compiexes, and quantitative extraction of the paraffin. All these operations, particularly when working with small quantities, unavoidably lead to appreciable errors. It should also be borne in mind that during decomposition of the hydrocarbon complex, stable colloidal dispersions are often formed, this being a reason for the partial loss of paraffin.

TABLE

Expt. No.	Designation of test paraffin	% Normal hydrocarbons (by adsorption analysis)	% Normal hydrocarbons, Hessler and Meinhardt method [10]	% Normal hydrocarbons by other methods
1	GOST (TU) 215-51, series 51-8, homogenized, m.p. 51°	86.5 (Solvent C_6H_6) 86.5 (Solvent CCl_4)	89.5	83 (Rosenberg's method [14]) 90 ($H_2SO_4 + P_2O_5$ [3])
2	GOST (TU) ORU 40-55 Paraffin, purified preparation for laboratory work	87.0 (Solvent C_6H_6) 87.0 (Solvent $C_6H_5CH_3$) 88.0 (Solvent CCl_4)	86.0	83 ($H_2SO_4 + P_2O_5$ [3])
3	GOST (TU) 215-51, series 52-5, homogenized, m.p. 50°	82.5 (Solvent C_6H_6)	81.0	–
4	GOST (TU) 215-51, series 52-113, homogenized, m.p. 51°	91.0 (Solvent C_6H_6)	90.0	–

In conclusion we should like to make the point that on the basis of the considerations advanced in this article, it should be possible to determine iso-hydrocarbons with weakly branched chains in paraffins. We hope to discuss this question separately.

SUMMARY

1. A study has been made of the adsorption on urea of benzene solutions of narrow fractions of normal hy-

drocarbons isolated from commercial paraffins. The experimental results obtained can be described by the Langmuir adsorption equation. Adsorption coefficients and the limiting value of the adsorption increase with increasing mean molecular weight of the fractions.

2. The adsorption isotherms of a number of commercial paraffins on urea have been studied, as well as those of paraffins purified from iso-paraffins; the adsorption experiments were carried out from solutions of these paraffins in benzene, toluene, and carbon tetrachloride for constant concentrations of the paraffin, and increasing amounts of urea (up to 12 g/g of paraffin). The isotherms of the purified paraffins terminate in a clearly defined horizontal section corresponding to complete adsorption of the dissolved paraffin, while the adsorption isotherms of the commercial samples, for equal additions of urea, terminate in linear sections inclined toward the abscissa; the latter testifies to the fact that the adsorption process is composed of two processes: adsorption of normal-hydrocarbons and adsorption of iso-hydrocarbons. It has been shown that the ordinate obtained by extrapolating the last inclined section of the isotherm to zero urea content is a measure of the content of normal-hydrocarbons in the test paraffin. The analytical results obtained in this way are independent of the nature of the solvent; this fact testifies to the reliability of the method.

3. The methods described in the literature for the determination of normal-hydrocarbons by means of urea give, as a rule, somewhat low results. These methods are equivalent, in essence, to the study of only one point on the isotherm, while a well-defined conclusion regarding the content of normal hydrocarbons in commercial samples can only be made, as is evident from the results of the work described here, on the basis of the study of all the adsorption isotherms.

4. The method suggested is simple from the experimental point of view; it can be carried out with small amounts of materials, and is based on the analysis of equilibrium solutions. Consequently, it is free from errors connected with the transfer, washing, and decomposition of the complex formed by the interaction of urea and the hydrocarbons.

LITERATURE CITED

[1] V.K. Tsiskovskii, Ts.N. Shcheglova and E.M. Nebylova, Chemistry and Technology of Fuel 6, 9 (1956).

[2] V.I. Isaguliants and G.M. Egorova, Chemistry of Petroleum* (State Fuel Tech. Press, 1949), p. 116.

[3] C. Kincannon and E. Manning, Ind. Eng. Chem. 47, 149 (1955).

[4] M.L. Konovalov, J. Russ. Phys. Chem. Soc. 37, 1119 (1905).

[5] S.S. Nametkin and S.S. Nifontov, Collection of Works, Vol. 2* (Izd. AN SSSR, 1955), p. 265.

[6] B.L. Moldavskii and S.E. Livshits, J. Gen. Chem. 5, 422 (1935).

[7] W. Leithe, Anal. Chem. 23, 493 (1951).

[8] H. Schindler and A. Kinsel, Petrol. Eng. 25, C-66 (1953).

[9] F. Cramer, Rev. Pure Chem. 5, 143 (1955).

[10] W. Hessler and S. Meinhardt, Fette u. Seifen. 55, 446 (1953).

[11] W. Schlenk, Lieb. Ann. 565, 204 (1949).

[12] V.G. Nikolaev, E.V. Zvereva, K.I. Zimna and Z.M. Popova, Chemistry and Technology of Fuel 3, 11 (1956).

[13] W. Hessler and G. Meinhardt, Fette u. Seifen. 55, 855 (1953).

[14] L.M. Rozenberg, I.S. Genekh and P.A. Nikitina, Azerbaidzhan Petroleum Economy 12, 18 (1953).

[15] A. Shamnan'ia, D. Lozh'e, I. Rolley and K. Verne, Technology of Treatment of Petroleum and Shale. IVth International Petroleum Conference, Volume IV* (State Fuel Tech. Press, 1956), p. 305.

[16] W. Zimmerschied, R. Dinerstein, A. Weitkamp and R. Marschner, Ind. Eng. Chem. 42, 1300 (1950).

*In Russian.

[17] P.P. Kobeko, Amorphous Substances* (Izd. AN SSSR, 1952), p. 271.

[18] A.Z. Golik and S.D. Ravikovich, Ukrainian Chem. J. 21, 39 (1956).

[19] S. Mumford, J. Chem. Soc. 4897 (1952).

[20] R. Scott and M. Magat, J. Pol. Sci. 4, 555 (1949).

[21] K. Van-Nes and K. Van-Vesten, Composition of the Lubricating Fractions of Petroleum and Their Analyses [Russian translation] (IL, 1954), p. 215.

[22] I. Kolthoff and A. Kahn, J. Phys. Coll. Chem. 54, 251 (1950).

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*In Russian.

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF NAPHTHALENE AND α- AND β-CHLORONAPHTHALENES

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The starting material for the synthesis of α-naphthyltrialkylsilanes is technical α-chloronaphthalene which, in addition to small amounts of naphthalene, contains about 10% β-chloronaphthalene. As a result of this, the synthesized product contains β-naphthyltrialkylsilane as an impurity in the α-naphthyltrialkylsilane. Direct synthesis is carried out at a high temperature and in the presence of catalysts which favor the isomerization of the α- and β-derivatives. Thus, in the final product obtained, the contents of the α- and β-isomers will depend on the conditions used for the synthesis. Accordingly, a method for the quantitative determination of mixtures of naphthalene, α- and β-chloronaphthalenes, α- and β-naphthyltrichlorosilanes, and α- and β-naphthyltrialkylsilanes is of practical interest.

The present article contains a description of a method we have developed for the quantitative determination of naphthalene, α- and β-chloronaphthalenes in each others presence. Since the chemical properties of the α- and β-isomers are very close to each other, a chemical analysis of mixtures of these isomers is very difficult. Zil'berman [1] and Wibaut [2, 3] have suggested determination of the α- and β-isomer contents in each others presence by melting point diagrams of binary mixtures of α- and β-chloronaphthalenes; this method, however, is very cumbersome and is not accurate enough. Moreover, the presence of free naphthalene in these mixtures complicates determination. Accordingly, for the analysis of mixtures of naphthalene, and α- and β-chloronaphthalenes, we used an ultraviolet spectrophotometric method. Characteristic absorption bands are observed in the ultraviolet absorption spectra of isomeric naphthalene derivatives (Table 1) [4, 5].

TABLE 1

Compound	Absorption maximum, in mμ	Compound	Absorption maximum, in mμ
α-Chloronaphthalene	314	β-Chloronaphthalene	320
α-Methylnaphthalene	314	β-Methylnaphthalene	319
α-Naphthonitrile	315	β-Naphthonitrile	324
α-Naphthol	314	β-Naphthol	325

It can be concluded from the results given in Table 1 that an absorption band is observed in the spectra of the α-isomers at 314 mμ, while in the case of the β-isomers, this band is displaced somewhat and is located at 320 mμ. This should permit identification of each isomer in a mixture. An absorption band is found at 310 mμ in the case of naphthalene itself; this should, accordingly, serve as a means of identifying naphthalene. The ultraviolet absorption spectra of naphthalene, and of α- and β-chloronaphthalenes are shown in the diagram.

The ultraviolet absorption spectra of the test materials were taken by means of a SF-4 quartz photoelectric spectrophotometer; the test materials were dissolved in absolute ethanol. The starting materials used for developing the quantitative method were: chemically pure naphthalene (m.p. 80.1°), chemically pure β-chloro-

Determination of naphthalene, and α- and β-chloronaphthalenes by an ultraviolet spectrophotometric method: ——) naphthalene; – – – –) α-chloronaphthalene; –·–·–·) β-chloronaphthalene.

naphthalene (m.p. 56°), and α-chloronaphthalene freed from β-chloronaphthalene as an impurity by a three-fold freezing out of technical α-chloronaphthalene.* The β-chloronaphthalene content of the α-chloronaphthalene was determined by means of melting point diagrams of binary mixtures of the α- and β-isomers. The results for the melting point diagrams for mixtures of α- and β-isomers were taken from the work of Wibaut and Bloem [2, 3, 6]. The content of residual β-chloronaphthalene in the α-chloronaphthalene did not exceed 2.7%. The boiling point of the purified α-chloronaphthalene was 121° at 12 mm residual pressure, while the setting temperature was −3.3°. Each test solution was tested for its conformity to the Beer law, for a concentration range from $1 \cdot 10^{-3}$ mole/liter to $5 \cdot 10^{-3}$ mole/liter in the wavelength region 310-320 mμ.

Since the test components of the mixture were found to conform to Beer's law, for the calculation of the content of each component, use was made of a formula relating optical density D of the mixture and the optical densities D_1, D_2 and D_3 of the components of the mixture in a definite spectral region,

$$D = D_1 + D_2 + D_3. \qquad (1)$$

Since D = Kcd, where K is the absorption coefficient of a mixture of the component, c is the concentration, and d is the thickness of the layer, then Formula (1) can be written in the form:

$$D = (K_1c_1 + K_2c_2 + K_3c_3)\,d. \qquad (2)$$

Having experimentally determined the values of the optical density of mixtures of the three components at wavelengths λ_1, λ_2 and λ_3, three equations can be compiled:

$$D_{\lambda_1} = (K_{1\lambda_1}c_1 + K_{2\lambda_1}c_2 + K_{3\lambda_1}c_3)\,d;$$
$$D_{\lambda_2} = (K_{1\lambda_2}c_1 + K_{2\lambda_2}c_2 + K_{3\lambda_2}c_3)\,d;$$
$$D_{\lambda_3} = (K_{1\lambda_3}c_1 + K_{2\lambda_3}c_2 + K_{3\lambda_3}c_3)\,d,$$

where $K_1\lambda_1$, $K_1\lambda_2$, $K_1\lambda_3$ are the absorption coefficients of the first component at λ_1, λ_2 and λ_3; $K_2\lambda_1$, $K_2\lambda_2$, $K_2\lambda_3$ are the absorption coefficients of the second component at λ_1, λ_2 and λ_3 and $K_3\lambda_1$, $K_3\lambda_2$ and $K_3\lambda_3$ are the absorption coefficients of the third component at λ_1, λ_2, and λ_3; c_1, c_2 and c_3 are the concentrations of the components of the mixtures; d is the thickness of the layer. Having experimentally determined the values of the optical density of mixtures at λ_1, λ_2 and λ_3, it is possible to calculate the concentrations c_1, c_2 and c_3, by solving the system of three equations with three unknowns. The values of the absorption coefficients of the components of a mixture at λ_1, λ_2 and λ_3 should be determined beforehand [7].

For the analysis of mixtures of naphthalene, and α- and β-chloronaphthalenes, the optical density of mixtures was measured at λ = 320 mμ (the absorption maximum for naphthalene), at λ = 314 mμ (the absorption maximum for α-chloronaphthalene) and at λ = 320 mμ (absorption maximum for β-chloronaphthalene). The values of the absorption coefficients of naphthalene, and of α- and β-chloronaphthalenes, at wavelengths of 310, 314 and 320 mμ (the so-called key absorption coefficients) were determined by measuring the optical density of solutions of the materials to be determined, at known concentrations of the latter, in the ultraviolet. Five solutions with varying concentrations of each test material were prepared and the mean values of the ab-

*The preparations of naphthalene, α- and β-chloronaphthalenes were kindly given to us by N.M. Przhiialgovskaia, a co-worker in the D.I. Mendeleev Moscow Chemicotechnological Institute (Department of Intermediate Products and Dyes).

sorption coefficients taken; the latter were calculated by means of the formula $K = D/cd$, where D is the optical density of the solution, c is the concentration in grams/liter, and d is the thickness of the layer in cm. The results obtained are summarized in Table 2.

TABLE 2

Compound	K_{310}	K_{314}	K_{320}
Naphthalene	1.842	0.543	0.136
α-Chloronaphthalene	2.061	2.083	0.889
β-Chloronaphthalene	1.451	1.021	1.940

On the basis of the mean values of the calculated key coefficients, three equations of the general type given below were obtained:

$$\frac{D_{310}}{d} = 1.842\ c_1 + 2.061\ c_2 + 1.451\ c_3,$$

$$\frac{D_{314}}{d} = 0.543\ c_1 + 2.083\ c_2 + 1.021\ c_3,$$

$$\frac{D_{320}}{d} = 0.136\ c_1 + 0.889\ c_2 + 940\ c_3,$$

where c_1, c_2 and c_3 are the concentrations of naphthalene, and α- and β-chloronaphthalenes respectively in the solution, in grams/liter; D_{310}, D_{314} and D_{320} are the values of the respective optical densities of the test solutions at 310, 314 and 320 mμ; d is the thickness of the layer in cm.

By means of these three equations, a determination of the concentrations of naphthalene, and α- and β-chloronaphthalenes when all three were present together was carried out; the mixtures were dissolved in absolute ethanol. For this purpose, three mixtures were prepared in which the concentrations of the various components were varied, and these concentrations determined by the ultraviolet spectrophotometric method.

TABLE 3

Composition of the mixture	Known concentration, in %	Calculated concentration, in %	D_{310}	D_{314}	D_{320}	Error, in %
Naphthalene	1.72	1.70	0.805	0.520	0.430	−1.16
α-Chloronaphthalene	1.30	1.32				+1.53
β-Chloronaphthalene	1.52	1.51				−0.65
Naphthalene	1.86	1.84	0.860	0.550	0.480	−1.07
α-Chloronaphthalene	1.30	1.24				−4.61
β-Chloronaphthalene	1.76	1.80				+2.27
Naphthalene	1.72	1.73	0.812	0.485	0.412	+0.58
α-Chloronaphthalene	1.15	1.15				0
β-Chloronaphthalene	1.76	1.74				−1.13

Table 3 contains the known and calculated values for the concentrations of the components in the mixtures, as well as the values of the optical density which were determined spectrophotometrically.

The results obtained show that the small amount of α-chloronaphthalene present as an impurity in the β-chloronaphthalene which was used for establishing the "key" coefficients, has only very little effect on the accuracy of the results obtained.

SUMMARY

A method has been developed for the quantitative determination of naphthalene, and α- and β-chloro-

naphthalenes; it is based on an ultraviolet spectrophotometric method in which the optical density of solutions of these compounds in absolute ethanol is measured at 310, 314 and 320 mμ.

LITERATURE CITED

[1] G.P. Zil'berman, V.G. Rashevskaia and V.V. Martyntseva, J. Appl. Chem. 9, 1832 (1936).

[2] J.P. Wibaut and G.P. Bloem, Rec. trav. chim. 69, 586 (1950).

[3] J.P. Wibaut, F.L.T. Sixma and T.F. Suyver, Rec. trav. chim. 68, 525 (1949).

[4] N.D. Coggeshall and A. Glesmer, J. Anal. Chem. 21, 550 (1943).

[5] L.N. Ferguson, Chem. Rev. 3, 385 (1948).

[6] N.M. Przhialgovskaia, Thesis, Mendeleev Moscow Chemicotechnological Institute (1953).

[7] Iu.Ia. Mikhailenko, Progr. Chem. 4, 443 (1947).

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SPECTROPHOTOMETRIC DETERMINATION OF CROTONALDEHYDE IN THE ULTRAVIOLET

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At the moment there is no satisfactory method for the quantitative determination of crotonaldehyde in the presence of other organic compounds such as acetaldehyde, acetone, acetylene, and acetic acid; it is precisely in such mixtures that crotonaldehyde occurs in the products of certain organic synthesis reactions, e.g., in the synthetic rubber industry. Existing methods [1, 2] which are based on the reactions of functional groups are not selective for crotonaldehyde, so that it is impossible to determine this aldehyde in the presence of unsaturated as well as carboxyl compounds. Naturally, the development of selective methods for the quantitative determination of crotonaldehyde is a real problem.

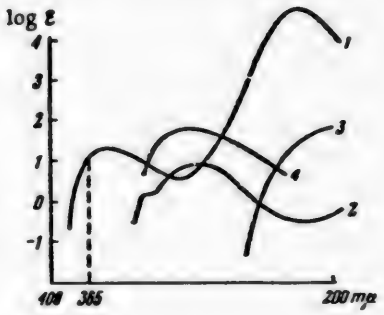

Fig. 1. Absorption spectra of solutions of crotonaldehyde (1), acetaldehyde (2), acetic acid (3), and acetone (4) in water.

The work described in the present article is one of the attempts made to solve this problem, the assumption made being that one approach should be photometric determination in the ultraviolet.

Solutions of crotonaldehyde in aqueous and nonaqueous media to which various amounts of acetaldehyde, acetic acid, acetone, and acetylene had been added were studied.

A comparison of absorption curves in the ultraviolet by crotonaldehyde, acetaldehyde, acetic acid, acetone, and acetylene (Fig. 1), taken from the literature [3], shows that at 365 mμ only crotonaldehyde absorbs. This means that it should be possible to determine crotonaldehyde photometrically without preliminary separation from the organic compounds listed above.

The work was carried out on a visual instrument suggested previously [4]. Quartz cells with a layer thickness of 25 mm were used.

The experimental technique consists of preparing various solutions with known contents of crotonaldehyde and measuring the optical density of the solutions. Each solution was diluted to half its original concentration (by addition of water or the appropriate solvent), and optical density measurements repeated. Such dilutions were repeated several times. The maximum crotonaldehyde concentration in aqueous solutions was 12.8% by volume, which is approximately equal to a saturated solution of crotonaldehyde in water.

Crotonaldehyde was prepared by dehydration of the aldol of orthophosphoric acid [5]; its boiling point was 101°, while n_D^{20} was 1.4364. According to published results the boiling point is 101.3-102.0° and n_D^{20} 1.4356 [6]. The crotonaldehyde content of the product obtained, as determined by the hydroxylamine-hydrochloride method [2] was 98.1%, while by the bromide-bromate method [7], its content was 99.1%.

Acetaldehyde was prepared by depolymerization of paraldehyde in the presence of concentrated sulfuric acid (b.p. 21°).

*N.M. Slastenova participated in the experimental work.

Acetone (analytical grade) and acetic acid (glacial) were the commercial products; the acetylene was taken from a cylinder.

Determination of Crotonaldehyde in Aqueous Solutions

First of all the concentration range over which aqueous solutions of crotonaldehyde conformed to Beer's law was established. The experimental results which are shown in Figure 2 indicate that this range is 0.1-12.8% by volume, accordingly, crotonaldehyde can be determined photometrically over this range.

TABLE 1

Effect of Acetaldehyde on the Optical Density of Aqueous Solutions of Crotonaldehyde

Crotonaldehyde, % by volume	Acetaldehyde, % by volume	Optical density
12.8	5.0;10.0;15.0;20.0;25.0	2.25;2.30;2.45;2.50;2.50
6.4	2.5; 5.0; 7.5;10.0;12.5	1.12;1.26;1.26;1.26;1.30
3.2	1.75;2.5;3.7;5.0;6.2	0.59;0.62;0.64;0.64;0.64
1.6	0.87;1.75;1.8;2.5;3.1	0.32;0.34;0.32;0.38;0.38
0.8	0.43;0.87;0.9;1.25;1.5	0.18;0.19;0.19;0.20;0.20
0.4	0.22;0.43;0.45;0.62;0.7	0.12;0.14;0.14;0.14;0.13
0.2	0.11;0.22;0.22;0.31;0.35	0.07;0.07;0.08;0.08;0.07
0.1	0.05;0.11;0.11;0.15;0.17	0.03;0.04;0.04;0.04;0.04

In order to establish the effect of acetaldehyde on the determination of crotonaldehyde in aqueous solutions, a series of tests was carried out with solutions of crotonaldehyde of different concentrations, to which acetaldehyde in amounts ranging from 5 to 25% by volume had been added.

A comparison of the results given in Table 1 with those shown on Figure 2 shows that the presence of acetaldehyde increases the optical density of crotonaldehyde solutions as compared with pure solutions of the latter, and this difference increases with increasing concentrations of acetaldehyde and crotonaldehyde.

Fig. 2. Relation between optical density and crotonaldehyde concentration.

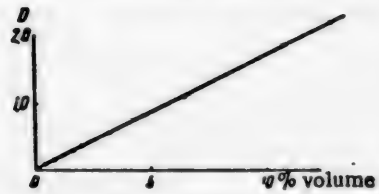

Fig. 3. Relation between optical density and crotonaldehyde concentration in acetaldehyde and acetone: x) solution of crotonaldehyde in acetone; o) solution of crotonaldehyde in acetaldehyde.

Next, a series of tests was carried out with solutions with low concentrations of crotonaldehyde, in order to establish the limits of applicability of the method for the determination of crotonaldehyde in the presence of acetaldehyde. These experiments showed that determination is possible for crotonaldehyde contents up to 0.4% by volume when the acetaldehyde concentration is not greater than 20% by volume; for a crotonaldehyde concentration of up to 1.6% by volume, the limiting concentration of acetaldehyde must be decreased to 15% by volume; while for a crotonaldehyde concentration of up to 3.2% by volume, the limiting acetaldehyde concentration should not be greater than 10% by volume.

In the case of low concentrations of acetaldehyde (below 5% by volume) and large concentrations of crotonaldehyde (above 3% by volume), as our experiments showed, the limiting concentration of acetaldehyde should not exceed 3.5% by volume; or more accurately, at crotonaldehyde concentrations up to 4% by volume, the maximum concentration of acetaldehyde which will not interfere with the determination is 5% by volume; while for crotonaldehyde concentrations up to 12.8% by volume, the limiting acetaldehyde concentration is 3.5% by volume.

Acetic acid starts to affect determination of crotonaldehyde when the concentration of the former exceeds 4.0% by volume for a crotonaldehyde concentration of 12.8% by volume, and affects

determination when its concentration is 10% by volume when the crotonaldehyde concentration is 3.2% by volume.

Acetone increases the results of determination slightly when solutions contain more than 2.0% by volume for a crotonaldehyde concentration of 12.8% by volume.

When all these compounds are present simultaneously, in the case where the concentration of the crotonaldehyde is at its maximum (12.8% by volume), the maximum permissible amounts of the impurities amount to 2.0% by volume acetaldehyde, 2.0% by volume acetic acid, and 1.0% by volume acetone.

Measurements of the optical density of aqueous solutions of crotonaldehyde and acetaldehyde, containing 6.0-0.4 and 3.0-16.0% by volume of these components, respectively, saturated with acetylene at atmospheric pressure and room temperature, showed that acetylene does not interfere with crotonaldehyde determination.

In order to check on the method, analyses were carried out on synthetic mixtures containing crotonaldehyde together with acetaldehyde, acetic acid, and acetone in aqueous solution (Table 2).

Determination of Crotonaldehyde in Nonaqueous Solutions

The optical density of solutions of crotonaldehyde in acetaldehyde and acetone almost coincides and is linearly dependent on the concentration over a wide range; this means that crotonaldehyde can be determined in these nonaqueous solvents (Figure 3).

TABLE 2

Determination of Crotonaldehyde in Synthetic Mixtures

Content in aqueous solution, in % by volume				Crotonaldehyde found, in % by volume
crotonaldehyde	acetic acid	acetone	acetaldehyde	
0.3	–	–	4.0	0.3
0.4	0.2	–	8.0	0.4
0.8	0.4	–	8.0	0.8
1.2	0.5	–	16.0	1.2
1.2	–	0.2	18.0	1.2
2.4	–	0.4	14.0	2.5
3.6	0.2	–	20.0	3.7
10.0	0.4	–	24.0	10.0

TABLE 3

Determination of Crotonaldehyde in Acetaldehyde

Crotonaldehyde taken, in % by volume	Crotonaldehyde found, in % by volume	Absolute error, in %
0.20	0.26	+0.06
0.40	0.40	–
0.50	0.54	+0.04
0.80	0.82	+0.02
1.00	1.02	+0.02

The results for determination of crotonaldehyde in acetaldehyde shown in Table 3 exhibit good agreement.

The presence of acetic acid in acetaldehyde or acetone strongly depresses the results for determination of crotonaldehyde; accordingly, these solvents should be free from acetic acid when they are to be used for crotonaldehyde determination. Acetylene does not interfere when these nonaqueous solvents are used, as in the case of aqueous solutions.

Irradiation for up to eight hours with ultraviolet does not affect the density of the working solutions.

SUMMARY

1. A method has been developed for the spectrophotometric determination in the ultraviolet of crotonaldehyde in the presence of acetaldehyde, acetic acid, acetone, and acetylene, in aqueous solutions.

2. Conditions for the photometric determination of solutions of crotonaldehyde in acetaldehyde, acetone, and acetic acid have been investigated.

LITERATURE CITED

[1] S.V. Alekseev, Synthetic Rubber 10, 13 (1936); R.B. Wearn, W.M. Murray Jr., M.P. Ramsey and N. Chandler, Anal. Chem. 20, 922 (1948); B. Wurzschmitt, Z. anal. Chem. 128, 549 (1948); D.W. Beesing, W.P. Tyler, D.M. Kutz and S.A. Harrison, Anal. Chem. 21, 1073 (1949); J. Mitchell Jr. and D.M. Smith, Anal. Chem. 22, 746 (1950); R.I. Veksler, Trans. Commission on Anal. Chem. Vol. III (VI) 1951, p. 369; M.P. Pool and A.A. Klose, J. Am. Oil Chemists Soc. 28, 215 (1951); J. Kubias and S. Pilny, Chem. Listy 47, 672 (1953).

[2] H. Schultes, Z. ang. Chem. 47, 258 (1934).

[3] Reference Book on Physicochemical and Technical Values, Vol. 2 [in Russian] (TE, 1932), p. 157; Landolt-Börnstein I, 3 (1951).

[4] K.P. Stoliarov and I.A. Stoliarova, J. Anal. Chem. 8, 33 (1953).•

[5] M.Ia. Kagan, G.D. Liubarskii and S.F. Fedorov, J. Appl. Chem. 7, 134 (1934).

[6] W.G. Young, J. Am. Chem. Soc. 54, 2498 (1932).

[7] A.I. Guliaeva, V.F. Polikaropova and Z.K. Remiz, Analysis of the Products from the Production of Divinyl from Ethanol by S.V. Lebedev's Method [in Russian] (Goskhimizdat, 1950), p. 190.

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BRIEF COMMUNICATIONS

POLAROGRAPHIC DETERMINATION OF ETHYL MERCURIC CHLORIDE IN GRANOSAN

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The possibility of reducing certain organometallic compounds on a dropping mercury electrode has been demonstrated by a number of authors [1-3]. In the work described here reduction of ethyl mercuric chloride (C_2H_5HgCl) on a dropping mercury electrode was studied, with the aim of determining this compound quantitatively in granosan (preparation NIUIF-2).

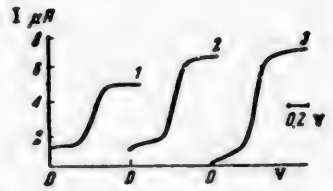

Fig. 1. Polarograms for the reduction of ethyl mercuric chloride in a supporting electrolyte of 0.2 N hydrochloric acid (Curves 1 and 2), and a polarogram obtained after treatment of granosan (Curve 3).

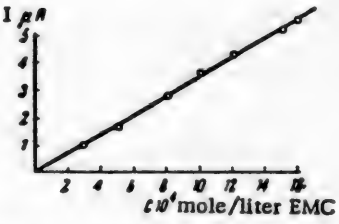

Fig. 2. Calibration line for determination of ethyl mercuric chloride in a supporting electrolyte of 0.2 N hydrochloric acid.

The work was carried out on a visual type polarograph of the Gorky Scientific Research Institute of Chemistry [4]; the mirror galvanometer used had a sensitivity of $0.6 \cdot 10^{-9}$ amp/mm/m scale reading. The characteristics of the capillary used were $m^{2/3} t^{1/6} = 2.48\ mg^{2/3} \cdot sec^{-1/2}$.

The ethyl mercuric chloride (EMC) used, which was twice recrystallized, had a melting point of 192°, in good agreement with the published results. A 0.005 M alcoholic solution of this compound was prepared from this product.

During a study of the reduction of ethyl mercuric chloride on a dropping mercury electrode in supporting electrolytes of HNO_3, HCl, KCl, KNO_3, and LiCl it was found that the best supporting electrolyte was 0.2 N hydrochloric acid. In this supporting electrolyte ethyl mercuric chloride gives clear-cut, well-defined waves at a half-wave potential of −0.4 volt relative to the saturated calomel electrode.

A calibration curve was used for obtaining quantitative characteristics. Solutions of ethyl mercuric chloride with concentrations ranging from $3 \cdot 10^{-4}$ to $1.5 \cdot 10^{-3}$ m/liter were prepared. The alcohol concentration was 30% in all the solutions. Solutions prepared in this way, after hydrogen had been bubbled through them, were then polarographed at a galvanometer sensitivity of S = 1/50.

In Figure 1 (Curves 1 and 2) are shown polarograms for ethyl mercuric chloride, while in Figure 2 is shown the calibration curve for its determination in a supporting electrolyte of 0.2 N hydrochloric acid.

Technical preparations of ethyl mercuric chloride may contain small amounts of mercuric chloride. During reduction of ethyl mercuric chloride and mercuric chloride in each others presence, two separate, well-defined curves are obtained, one of which corresponds to the reduction of mercuric chloride and starts at zero applied emf, while the other corresponds to the reduction of ethyl mercuric chloride (Figure 3, Curve 1). The mercuric chloride concentration was changed from $1.6 \cdot 10^{-5}$ to $1.6 \cdot 10^{-4}$

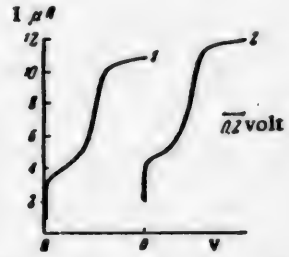

Fig. 3. Polarogram for ethyl mercuric chloride and mercuric chloride in a supporting electrolyte of 0.2 N hydrochloric acid (Curve 1), and the polarogram for a solution obtained after treatment of granosan to which mercuric chloride was added.

m/liter, while the concentration of ethyl mercuric chloride was kept constant at 0.002 m/liter.

For a mercuric chloride content which was one-tenth to one-hundredth of the ethyl mercuric chloride, the diffusion current of the latter was found to be independent of the mercuric chloride concentration. When, however, both components were present in approximately equal amounts – and particularly when there was more mercuric chloride present than ethyl mercuric chloride – the diffusion current of ethyl mercuric chloride increased considerably with increasing mercuric chloride concentration.

Ethyl mercuric chloride does not affect the diffusion current of mercuric chloride. When polarograms were taken of solutions with a constant concentration of mercuric chloride of $0.8 \cdot 10^{-3}$ m/liter, and with varying concentrations of ethyl mercuric chloride, the diffusion current of mercuric chloride remained constant, while that for ethyl mercuric chloride was directly proportional to the concentration of the latter.

Since the amounts of mercuric chloride which are present in granosan are small, simultaneous determination of ethyl mercuric chloride and mercuric chloride is completely possible.

Granosan is a finely-ground mixture of technical talc and ethyl mercuric chloride. The latter is quantitatively extracted from granosan with ethanol by refluxing on a water bath (Table 1).

TABLE 1

Ethyl mercuric chloride added to the talc, in g	Ethyl mercuric chloride determined polarographically, in g	Error, in %
0.0132	0.0145	+9.8
0.0172	0.0165	−4.0
0.0288	0.0397	+2.3
0.0306	0.0311	+1.6

TABLE 2

Granosan sample 1799		Granosan sample 1800	
sample weight, in g	ethyl mercuric chloride found, in %	sample weight, in g	ethyl mercuric chloride found, in %
3.0074	1.64	3.0001	1.69
3.0029	1.71	3.0009	1.71
2.0006	1.61	2.0004	1.82

Mercuric chloride can be determined at the same time as ethyl mercuric chloride. Nevertheless, when polarograms were taken of solutions obtained by extraction of ethyl mercuric chloride from granosan, the wave for mercuric chloride was not observed (Figure 1, Curve 3).

Experimental procedure for determination of ethyl mercuric chloride. 3 g of granosan and 25-30 ml of ethanol were refluxed in a round-bottom flask on a water bath for ten minutes. After cooling, the residue was filtered off and washed a few times with hot alcohol and the filtrates collected in a standard flask; when the temperature was 20° the volume was made up to the mark with alcohol. 2 ml of this solution was placed in an

electrolyzer and 3 ml of 0.3 N hydrochloric acid added; after the solution had been purged with hydrogen for 30 minutes, polarograms were taken at S = 1/50. The concentration of ethyl mercuric chloride was then determined by means of the calibration curve. Satisfactory results were obtained during determination of ethyl mercuric chloride in production samples of granosan (Table 2). A gravimetric method, GOST-5150-49, gave higher results because technical talc usually gives a solid residue (an increase in weight) of up to 0.35%, presumably elemental sulfur.

SUMMARY

Reduction of ethyl mercuric chloride on a dropping mercury electrode has been studied and conditions have been established for its quantitative determination in granosan. Conditions have been found for the simultaneous, quantitative determination of ethyl mercuric chloride and mercuric chloride.

LITERATURE CITED

[1] G. Costa, Gazz. chim. ital. 80, 42 (1950).

[2] G. Costa, Ann. Chim. applicata 38, 665 (1948).

[3] V.F. Toropova and M.K. Saikina, Collection of Articles on General Chemistry, 1 [in Russian] (Izd. AN SSSR, 1953), p. 310.

[4] I.A. Korshunov and A.P. Rostokin, Factory Labs. 12, 373 (1946).

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A QUALITATIVE REACTION FOR META-AMINOPHENOL AND PARA-AMINOSALICYLIC ACID

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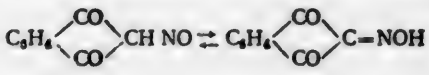
We have observed that on heating a solution of meta-aminophenol in glacial acetic acid with 2-nitrosoindanedione-1,3, a green fluorescence appears. When the concentration of the meta-aminophenol in solution is high enough, a red color appears. When the meta-aminophenol concentration is very low, the fluorescence only appears on cooling the solution. A small excess of nitrosoindanedione (up to three moles per mole of meta-aminophenol) favors the reaction; a large excess of this reagent, however, decreases the sensitivity of the reaction.



The limiting dilution of meta-aminophenol at which the fluorescence is still observable is 1:40,000. In solution in ethanol, ether, benzene, dioxan , dilute acetic acid, and also in glacial acetic acid containing a small amount of acetic anhydride, the fluorescence does not appear.

Ortho-aminophenol and para-aminophenol do not give this reaction, and do not interfere when they are present in amounts which are one-hundred times that of the meta compound. When large amounts of the ortho- and para-compounds are present, the solution becomes intense-red and the fluorescence does not appear. The following compounds do not give a green fluorescence with nitrosoindanedione: phenol, resorcinol, aniline, and many other aromatic and aliphatic primary, secondary and tertiary amines; this reaction therefore appears to be specific for meta-aminophenol.

Para-aminosalicylic acid (PASA) on heating is readily decarboxylated to give meta-aminophenol. Accordingly, one might expect that PASA would also give a positive reaction with nitrosoindanedione. In fact, when PASA is heated in glacial acetic acid with nitrosoindanedione, carbon dioxide is liberated and the liquid gradually acquires a green fluorescence. Since decomposition of PASA does not occur immediately, in the case of low concentrations of PASA, it is necessary therefore to prolong the heating. The limiting dilution of PASA at which fluorescence can be detected is 1:28,000. The ratio of the limiting sensitivities of meta-aminophenol and PASA (40,000:28,000) corresponds approximately to the inverse ratio of their molecular weights (153:109), from which it follows that PASA almost quantitatively decomposes to give meta-aminophenol under the reaction conditions used.

Preparation of Nitrosoindanedione

1. Rapid preparation of small amounts [1]. Indanedione-1,3 is dissolved in aqueous alkali, a solution of sodium nitrite is added and the mixture slowly poured into dilute sulfuric acid. The precipitate which settles out is crystallized from glacial acetic acid.

2. Preparative method [2]. To 8 g of indanedione in 300 ml of dilute alkali contained in a flask provided with a mechanical stirrer is added 4 g of sodium nitrite. The flask is cooled with ice, and hydrochloric acid added dropwise with constant stirring until the reaction mixture gives an acid reaction. The mixture is then agi-

tated at room temperature for a further 45 minutes. The precipitate which separates out is recrystallized from glacial acetic acid. The yield is 8.4 g of nitrosoindanedione (87% of theory); the compound is in the form of yellow crystals with a melting point of about 200°; the melting point depends partly on the rate of heating [3], and also on the solvent used for its recrystallization [4]. Small amounts can be recrystallized from water as well.

The color reaction itself. 2-3 mg of meta-aminophenol is dissolved in 5 ml of glacial acetic acid, and a few milligrams of nitrosoindanedione is then added and the mixture boiled for one minute; the mixture is finally cooled under the tap. A green fluorescence should appear. For smaller amounts of meta-aminophenol, heating should be continued for a longer time. During detection of PASA in the same way, heating should also be carried out for a longer time; for limiting concentrations of PASA, this period should be as much as ten minutes.

SUMMARY

Meta-aminophenol and para-aminosalicylic acid give a green fluorescence on heating in glacial acetic acid with nitrosoindanedione.

LITERATURE CITED

[1] W. Wislicenus, Ann. 246, 353 (1888).

[2] W.O. Teeter and R.L. Shriner, J. Am. Chem. Soc. 55, 3026 (1933).

[3] G. Wanag and A. Lode, Ber. 72, 49 (1939).

[4] E.Iu. Gudrinietse and G.Ia. Vanag, J. Gen. Chem. 24, 725 (1954).*

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COLOR REACTIONS OF PHENOLS WITH XANTHYDROL

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Xanthydrol is normally used as a reagent for establishing the identity of amines, urethanes, and barbituric acid derivatives [1]. With these classes of compounds xanthydrol forms xanthyl derivatives which can be readily purified, and have sharp melting points. Xanthydrol is also known to react with mono- and diphenols [2, 3], colorless, crystalline condensation products being formed. This latter reaction is of no analytical significance since it proceeds very slowly and gives a small yield of final products which are rather difficult to isolate and purify.

We were the first to observe that xanthydrol in alcoholic solution, in the presence of mineral acid, is capable of reacting with phenols to give colored products. The color reaction of xanthydrol with phenols is more specific than the well-known reaction with ferric chloride. Many phenol derivatives which give colored products with the latter reagent do not react with xanthydrol.

Xanthydrol was prepared by the reduction of pure xanthone by means of sodium amalgam [4]. The damp preparation was dried at 40-50° to constant weight and then dissolved in alcohol. The reagent was found to be still usable after six months storage.

The reaction between phenols and xanthydrol is best carried out as follows. 2-3 mg of test material is introduced into a test tube and 0.5 ml of a 5% solution of xanthydrol in alcohol added. The mixture is gently warmed to dissolve the phenol, and two drops of dilute or concentrated hydrochloric acid added; the contents of the test tube are then boiled for several seconds. Intense colors should then develop.

On heating the xanthydrol solution with two drops of hydrochloric acid a yellow color appears which disappears on cooling the reaction mixture. The color obtained on heating a phenol with xanthydrol and hydrochloric acid, however, is very stable and there is no decolorization even after several days.

Colors of the Reaction Products Formed from Phenols and Xanthydrol in the Presence of Hydrochloric Acid

Test compound	Color	Sensitivity, in γ/ml	Test compound	Color	Sensitivity, in γ/ml
Phenol	Raspberry-red	25	Guaiacol	Violet-red	50
α-Naphthol	Dark green	5	Resorcinol	Blue-violet	10
β-Naphthol	Grass-green	10	Hexylresorcinol	Dark blue	–
o-Cresol	Bright red	4	Hydroquinone	Yellow-green	25
m-Cresol	Orange-red	5	Pyrogallol	Violet-red	2.5
Thymol	Wine-red	10	Phloroglucinol	Violet-blue	10
Carvacrol	Red	8	Tannin	Violet-red	–
Eugenol	Brown-red	–	Methyl salicylate	Rose	–
Pyrocatechol	Lilac	10			

The table contains the results obtained for the phenols which we studied. The reaction sensitivity increases sharply with decreasing pH of the reaction mixture. The reaction sensitivity was established as follows. 0.4 ml

of an alcoholic solution of a phenol of an appropriate concentration was introduced into a test tube; this was followed by 0.4 ml of xanthydrol solution and 0.2 ml of hydrochloric acid (sp.gr. 1.18). The mixture was boiled for several seconds. After cooling, the color of the reaction mixture was noted.

It is evident from the table that not only unsubstituted phenols react with xanthydrol, but also their derivatives containing: a) alkyl groups (cresols, thymol, carvacrol, eugenol, hexylresorcinol); b) methoxy groups (guaiacol); and c) an ester group (methyl salicylate).

Color reactions with xanthydrol are not given by phenol derivatives containing: a) acid groups (salicylic acid, gallic acid, β-naphthol-3,6-disulfonic acid, 3-acetamino-4-hydroxyphenylarsonic acid); b) basic groups (p-aminophenol, adrenaline); c) halogens (tribromophenol); and d) nitro-groups (o- and p-nitrophenol, 2,4-dinitrophenol, and picric acid).

SUMMARY

Xanthydrol in alcohol solution, on being heated with phenols in the presence of hydrochloric acid gives colored products. This reaction can be used for identifying phenols. Reactions between xanthydrol and 17 phenols are described and the reaction sensitivity of most of them determined. Unsubstituted phenols and phenol derivatives containing alkyl or methoxy groups give a positive reaction with xanthydrol. Phenol derivatives containing halogens, carboxy, amino, and nitro groups do not give this reaction.

LITERATURE CITED

[1] V. Johnson, R. Shannon and R. Reid, Organic Reagents for Organic Analysis [Russian translation] (Moscow, 1948), p. 115.

[2] I.B. Niederl and W.F. Hart, J. Amer. Chem. Soc. 59, 719 (1937).

[3] R. Fabre, Ann. Chim. [9] 18, 49 (1922).

[4] Syntheses of Organic Preparations, Collection [in Russian] (Moscow, 1949), p. 234.

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THE USE OF A DC CURRENT FOR CERTAIN CHROMATOGRAPHIC STUDIES

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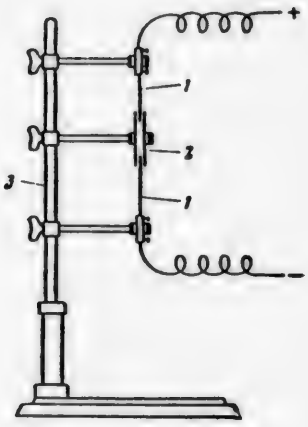
In the presence of a conducting medium in a column containing a sorbent with an appropriate reagent, it is possible to increase the sensitivity of the chromatographic method of detecting certain ions by passing a dc current through the column.

Into one end of the column packed with sorbent is passed a known amount of test solution and developer-reagent. When the solution does not moisten the contents of the column, the other end of the latter is placed in a small beaker, on the bottom of which is placed a filter paper soaked with distilled water. The water rises in the tube and, in the course of 10-15 minutes, moistens the sorbent. The tube is then fixed in a stand and two platinum needles are fitted into the column packing from both ends (diagram). Since the electrical conductivity of the column is very small, it is necessary to push the needles to a distance of not more than 1-1.5 cm into the sorbent. The platinum needles are connected to a dc supply with a fairly high voltage of 15 volts, sometimes even as high as 25 volts.



It is essential to remember that the experiments are being carried out with a weak current. The best results are obtained with a current of 0.01-0.02 amp. Increasing the current considerably led, in most cases, to uneven development of some parts of the column and, sometimes, even to the appearance of a noncharacteristic dark brown color.

Such a phenomenon was observed during detection of NO_2^- with *a*-naphthylamine.

When the technique described was used, positive results were obtained when the anode needle was placed into that end of the tube containing sorbent, through which the test solutions and developers were passed.

Using this technique experiments were carried out on the detection of several anions. In our studies the best results were obtained during the detection of NO_2^-.

Detection of NO_2^- by Formation of Azo Dyes

The amino compounds used were sulfanilic acid, p-nitroaniline and sulfanilamide, while the azo components used were *a*-naphthol, *B*-naphthol and *a*-naphthylamine. The sorbents used were chemically pure SiO_2 and Al_2O_3 which had been finely ground (sieve with 0.10 m/m mesh); it was found that SiO_2 was a better sorbent than Al_2O_3 from the point of view of sensitivity.

1) For the detection of NO_2^-, one part of *a*-naphthylamine, one part of sulfanilic acid, and ten parts of SiO_2 were mixed. 0.05 ml of the test solution was introduced by means of a micropipet into the packed column; this was followed by 0.05 ml of 5 N CH_3COOH. A red band was formed. The limit of identification of NO_2^- was found to be 0.01 γ NO_2^-. An electric current (voltage up to 25 volts) enhanced the intensity of the color but the

sensitivity remained almost the same.

2) For detection of NO_2^- with sulfanilamide and α-naphthylamine, using SiO_2 as sorbent (ratio 1:10), the limit of identification without using a current was found to be 0.04 γ NO_2^-, whereas when a current was used, the limit was found to be 0.02 γ NO_2^-. When a current was used the intensity of the color also increased, even at the limits of the first limit of identification of 0.04 γ. A red band was observed.

3) For detection of NO_2^- with sulfanilic acid and α-naphthol, and using Al_2O_3 as sorbent (in the proportion of 1:10), 0.05 ml of test solution was introduced into the column first; this was followed by 0.05 ml of 5 N CH_3COOH. A rose color was first formed, which subsequently changed to orange. The limit of identification without using a current was 0.12 γ NO_2^-, while on using a current (20 volts) the limit was 0.05 γ NO_2^-.

4) When detection of NO_2^- was carried out using sulfanilic acid and β-naphthol, and SiO_2 was used as the sorbent (in the proportion of 1:10) an orange band was formed. The limit of identification was 0.16 γ NO_2^-. Passage of an electric current had little effect on the reaction sensitivity.

5) For the detection of NO_2^- with p-nitroaniline and β-naphthol using SiO_2 as sorbent (in the proportion of 1:20), the limit of identification without a current was 0.2 γ NO_2^-, while with a current (15-20 volts) the limit was 0.08 γ NO_2^-.

6) Detection of NO_2^- with p-nitroaniline and β-naphthol, using SiO_2 as sorbent (in the proportion of 1:20), was less sensitive. The limit of identification without using a current was 1 γ NO_2^-, while with a current (15-20 volts) it was 0.16 γ NO_2^-. A red band was formed.

The enhanced sensitivity of the reactions indicated above when a dc current is used is, presumably, connected with the concentration of the reactants in the zone surrounding the anode.

SUMMARY

The sensitivity of the chromatographic method for detecting NO_2^- ions with sulfanilamide and sulfanilic acid can be increased by passing a dc current through a column packed with sorbent containing the appropriate reagent, as long as the column contains a medium which is conducting.

Received August 2, 1956

PETR ANDREEVICH VOLKOV

(October 1, 1889 – October 26, 1957)

Petr Andreevich Volkov was born on the 21st of October, 1889 in Cherepovets, Novgorod region; he finished at the chemical section of the Leningrad Polytechnical Institute in 1921.

From 1918 Volkov worked in the Academy of Sciences, starting in the Commission of Natural Resources (KEPS); he then transferred to the Radium College (KEPSe), which was changed to the State Radium Institute in 1922. In 1929 Volkov joined the Institute of Geological Sciences where he worked as a senior scientific worker till his death.

In 1936 he was awarded the degree of candidate of chemical sciences without defending his thesis. For carrying out government work he was awarded the order of the "Sign of Honor," and was awarded the order of Lenin for his long years of service.

Volkov was an outstanding analytical chemist and a talented technologist. Starting off with the solution of problems of an analytical and preparative character, Volkov applied them on a plant scale.

He was one of the pioneers of radium technology in Russia. His first scientific work was devoted to a study of equilibrium in solutions of barium and lead chlorides, and was carried out under the direction of V.G. Khlopin and N.S. Kurnakov. His important work on obtaining preparations containing a high percentage of radium formed a basis for a radium bank in the Radium Factory, in whose construction he took a leading part; he also organized a mine laboratory which he managed for two years (1924-1926).

He carried out a large amount of analytical work on ores and shales, and discovered and described a new mineral "tangeite."

From 1926 to 1934 Volkov occupied himself with problems relating to sulfur, and from 1933 to 1941 developed the technology of the Khibinsk ores; this included: methods of breaking down nepheline with sulfuric and sulfurous acids for the preparation of silica-gel and alum, a method for preparing the rare earths from lovchorite and apatite, and a method for extracting CaO from apatite, etc.

During the Second World War Volkov was head of the analytical laboratory of the Ural Branch of the Academy of Sciences in Sverdlovsk, while from 1944 onward he was at the Central Chemical Laboratory of the Institute of Geological Sciences.

Since 1946 Volkov has been engaged in special Government work, and carried on with this work until his death. Under his direction, methods were developed for the determination of small amounts of impurities in pure metallic uranium and, in conjunction with his students, he personally developed a neat and simple method of determining uranium which is characterized by high accuracy and the speed with which it can be carried out. This method is widely known in practice as "Volkov's Method."

There was nothing stereotyped about his work; the creative element was always present. He always shared his ideas, successes and failures with his comrades, and was never satisfied with what he had achieved, but always strove for perfection.

He turned his ideas to practical use by stubborn work, and by an infinite amount of experimental work, and succeeded in making things work which at first glance would seem to be impossible.

Although he was deeply interested in his work, outside the laboratory Volkov was a sociable, interesting person. He enjoyed the sincere respect and love of his companions at work and of numerous students.

L. Borneman

THE FOURTH CONFERENCE ON THE ANALYSIS OF THE NOBLE METALS

May 20-23, 1957

The Fourth Conference on the Analysis of the Noble Metals was held on May 20-23, 1957, in Sverdlovsk; it was convened by the N.S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences and by the Factory on the Treatment of Noble Metals, in conjunction with the Ministry of Finance of the USSR, the Ministry of Non-Ferrous Metals of the USSR, and by the Ural House of Technics. One hundred and eleven delegates participated. Thirty-two organizations were represented, while thirty-five reports and communications were read.

One section of the reports was devoted to questions on technical methods of analysis: "The Use of Thionalide and Thiourea for Determination of Rhodium and Iridium," by N.K. Pshenitsyn and L.V. Prokof'eva; "Recent Advances in the Chemical Analysis of Factory Materials," by Kh.I. Tsybulevskii and I.N. Firsova. This question was also dealt with in reports from representatives of various factories (M.S. Usova et al.). Several reports dealt with volumetric methods: "Volumetric Determination of Iron, Platinum and Iridium in Each Others Presence," by A.A. Grinberg; "A New Volumetric Method for the Determination of Silver in Alloys and Production Residues," by M.A. Chentsova, T.P. Iufa and V.G. Levian, etc.

A special session was devoted to spectrographic methods of analysis used at present in all refining factories. The reports of V.P. Khrapaia, V.L. Ginsburg, A.D. Gut'ko and N.N. Pankratov, A.D. Kuranov, N.P. Ruksh, M.M. Sviridova were devoted to the determination of all the noble metals, and of some impurities in concentrates, alloys, ores, and other materials. Some reports dealt with the preparation of poor samples for spectrographic analysis (S.M. Anisimov, K.A. Pomytov and E.I. Nikitina, N.L. Chentsova).

The applicability of assay methods (cupellation as a silver bead) for the determination of rhodium, iridium and ruthenium in ores and other products was discussed. In some instances, these elements are not concentrated completely in the silver bead. It turned out from the discussion that the method of copper assay as applied to materials containing iridium, rhodium or ruthenium has not been developed sufficiently (the report of S.K. Shabarin and L.D. Fridman).

Four reports dealt with polarographic methods and ion exchange: "A Polarographic Method of Determining Iridium," N.K. Pshenitsyn, N.A. Ezerskaia and V.D. Ratnikova; "Determination of Lead, Bismuth and Antimony in Refined Gold," E.K. Kuznetsova; "Methods of Determining Impurities in Platinoid Materials Based on Ion Exchange and Polarography," S.M. Anisimov, V.M. Klypenkov, P.G. Shulakov, V.N. Alianchikova and P.A. Gurin; and "Polarographic Determination of Some Platinum Metals on Solid Electrodes," Iu.S. Lialikov and M.B. Bardin.

A group of reports dealt with spectrophotometric and photocolorimetric methods of analysis: "Photocolorimetric Methods of Analyzing Platinum Metals (Refined)," V.K. Levian and T.P. Iufa; "A Study of Certain Spectrophotometric Methods of Determining Iridium and the Reactions Forming the Basis of these Methods," N.K. Pshenitsyn, S.I. Ginsburg and L.G. Sal'skaia; "A Photocolorimetric Method of Determining Rhodium in the Presence of Platinum," V.N. Aleksandrov; "Photocolorimetric Determination in the Presence of Silver," V.F. Barkovskii.

Two reports were given by V.B. Avilov – "Chromatographic Determination of Gold," and the "Effect of Complex Formation and the Acid-Alkali Equilibrium of the Medium on the Potentials of Systems."

The communication of V.V. Kosova and that of S.M. Anisimov, V.M. Klypenkov and V.P. Tsimbal dealt with the electrometric determination of silver in alloys and factory products.

M.S. Ruzhinkov demonstrated a technique for the determination of gold on a touchstone which has been used for several centuries, and gave details of a new method for testing palladium alloys on a touchstone.

Finally, the last group of reports dealt with physical methods of analysis: "Determination of the Chemical Composition of Ternary Alloys on the Basis of Physical Properties," A.A. Rudintskii; "Determination of the Chemical Composition of Binary Alloys on the Basis of EMF," A.P. Adakhovskii and V.M. Karbolin; "Quantitative Determination of Micro Amounts of Gold and Platinum Metals by a Radioactivation Method," A.I. Kulak and O.E. Zviagintsev; and "Apparatus and Methods for the Determination of Gases in Metals," Z.M. Turovtseva.

A report was finally given by D.G. Grebenkin a representative of the Ministry of Finance of the USSR on "The Role and Importance of Analysis in Production Control."

Many of the reports led to questions and discussions. The Conference adopted a resolution noting the achievements and gaps in the analysis of noble metals during the last two-and-a-half years; the Conference indicated what further work should be carried out in this field.

The Conference adopted a resolution to the effect that the reports should be published as soon as possible.

O.E. Zviagintsev

SYMPOSIUM ON THE THEORY AND APPLICATION OF COMPLEXONS IN ANALYTICAL CHEMISTRY

A symposium on the theory and application of complexons in analytical chemistry was held in Moscow on November 28-30, 1957. The symposium was convened by the Commission on Analytical Chemistry of the V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, in accordance with the wishes expressed a year previously at the All-Union Conference on the application of organic reagents in analytical chemistry. More than 50 specialists in the field of complexometry participated in the symposium; these included representatives from the social democracies: R. Pribil and I. Kerbl (Czechoslovakia), L. Erdei (Hungary), Lian Shi-Tsuan and Tsen In-Tsao (China), Tutundzhich (Yugoslavia) and others. Thirteen reports were read; some of the reports were devoted to theoretical questions – the thermodynamic stability of complexes, the effect of molecular structure on indicator color, etc. Some attention was given to the synthesis of new complexons and color indicators, and also to the application of complexons, in particular, the use of Complexon III, for the separation (for example, with the aid of ion-exchange chromatography) and determinations of elements.

The communication of K.B. Iatsimirskii (Ivanovo) dealt with the results of a thermochemical study of complex compounds. Complexonates differ from other complex compounds in that the formation of the former is weakly exothermic or even endothermic. The author attributes the stability of the complexes to a decrease in entropy of the system and, from the viewpoint of the chemical process, by the fact that during complex formation, there occurs liberation of water molecules from the hydrated layer of the cation, followed by disorientation of these molecules. It was pointed out that when using an indicator, the rate of formation of the complex should be borne in mind. Thus, indicators are not suitable for elements which react slowly.

Color indicators play an important role in complexometry. Metallochrome indicators of the phthalein series and two new indicators – glycinethymol blue and glycinecresol red – were discussed in the report by R. Pribil (Prague). The author showed that glycinethymol blue gives an intense color with copper at pH 5-6, which is of a deeper blue than that of the complex formed between copper and ammonia. During titration with Complexon III, the color of the solution changes from blue to lemon-yellow. This indicator can also be used successfully in photometry. The other indicator – glycinecresol red is also suitable for copper determination. The color changes from red to yellow in this case. The author also gave some results on the application of other indicators – nitroazobenzopyrocatechin and sulfoazopyrocatechin, aminopropionic acid derivatives, and glycinenaphthol violet. The author demonstrated some experiments on titration with the new indicators.

I. Kerbl (Prague) communicated some results of a study of metallochrome derivatives of amino acids, and on the mechanism of metallochromic indicators. The capacity of an organic compound to bind cations is attributed by the author to the structure of the molecule and to the deformation of the electronic layers of the cation. The appearance of a color is also possible in the case of cations in which the electronic layers are not deformed (e.g., colorless ions). One of I. Kerbl's reports was devoted to titration error in complexometry.

The use of certain new indicators in complexometry was the subject of the reports given by L. Erdei (Budapest) and I.M. Mustafin (Saratov). The new indicator variamine was dealt with in the first report. This indicator gives a color change on changing the ratio of the components in the system ferricyanide-ferrocyanide (at pH 5), and this in turn shifts on the appearance or disappearance of ions of zinc, lead and others during titration with ethylenediaminetetracetic acid. The author demonstrated a very effective experiment in which a chemiluminescent indicator – luminol and hydrogen peroxide – was used for the determination of copper. Luminol and hydrogen peroxide give a luminescence which becomes weaker on addition of copper. During titration of such a solution with Complexon III the copper is complexed and the luminescence intensity increases; determination

of copper is based on this fact. I.M. Mustafin's report demonstrated the possibility of using phenolcarboxylic acids of the triphenylmethane series as complexonometric indicators. The author has used these indicators for the determination of a number of cations: Be^{2+}, Mg^{2+}, Al^{3+}, Ni^{2+}, VO^{2+} etc. The compounds formed thereby are readily soluble in water and have an intense blue color. Some of the colored compounds are destroyed by solutions of complexons. The author demonstrated some experiments in which the new indicators were used.

A report by R. Pribl dealt with the complexonometric determination of oxidizing and reducing materials. The author uses the indicator xylene orange for this purpose. The report demonstrated the possibility of carrying out direct titration of mercury, zinc, lead, cadmium, bismuth, indium, and also the possibility of determining gallium, iron, copper, uranium, vanadium, chromium, aluminum, and tin. Thus, for the determination of vanadium, the latter is reduced with excess ascorbic acid which is complexed with Complexon III, excess of the latter being then titrated with thorium in the presence of an indicator. The author indicated the possibility of a photometric determination or a qualitative detection of trivalent uranium by means of indicators with which uranium gives very stable complexes not suitable for titration.

The report of P.N. Palei (Moscow) was devoted to the reducing properties of Complexon III. He showed that in acid media, under the influence of an oxidizing agent, the molecule of Complexon III undergoes a breakdown in which four molecules of CO_2 are liberated. The author was of the opinion that it is the COOH groups that break down. The report contained examples of the reduction of plutonium, vanadium, and chromium by Complexon III.

Exploratory work in the synthesis of new complexons and the study of their behavior was the subject of R.P. Lastovskii's report (Moscow). The use of a new fluorescent complexon — tetracetic acid - acridine yellow — was described in this report. This complexon is very suitable for paper chromatography (for example, for the separation of barium and strontium from calcium and magnesium). The author has also synthesized hexamethylenetetracetic acid which can mask iron without masking nickel and cobalt; and also parafuchsinhexacetic acid by means of which lead can be determined as an impurity in the presence of titanium. The author demonstrated the possibility of carrying out a polarographic determination of neodymium, lanthanum, and gadolinium by means of this last complexon.

In the report by Lian Shi-Tsuan and Tsen In-Tsao (Peking), which was devoted to the possibility of using complexes of pyrocatechin with trivalent iron for the determination of fluorine, results were given of the discovery of two more complexes in addition to the three already known. The authors showed that in the pH range 4.2-10, fluorine does not decolorize the complexes of pyrocatechin with iron (III), i.e., these complexes are more stable than the complex $[FeF_6]^{3-}$. Over the range pH 2-4, however, the complex $[FeF_6]^{3-}$ is the most stable.

The application of complexons in ion exchange was dealt with in the report given by M.M. Seniavin (Moscow). The high complexing capacity of the complexons allows them to be used successfully for chromatographic separation, for example, of the alkali metals. The author pointed out an interesting characteristic of the complexons — their bifunctionality, i.e., their capacity to form complex compounds with a bond through an oxygen or nitrogen atom; separation of mixtures of the rare earths by using inhibitor ions is based on this fact.

Analytical methods in nonferrous metallurgy based on the use of Complexon III was the subject of Iu.Iu. Lur'e's report (Moscow). The author gave several examples of the advantages of complexometry over other titrimetric methods such as iodometric, chromatometric methods, etc. Complexon III has been used successfully for phase analysis.

In the discussion that followed, A.K. Babko suggested the addition of Complexon III for slowing down crystallization processes. Thus, zirconium phosphate in the presence of Complexon III precipitates slowly without trapping titanium; the precipitate is readily filtered.

I.P. Alimarin, I.V. Tananaev, V.I. Kuznetsov, A.K. Babko and N.P. Komar et al. took an active part in the symposium.

Similar conferences in which both Soviet and foreign scientists take part, in addition to establishing friendly contacts, can, to a significant extent, help in the solution of new problems in analytical chemistry.

A.A. Pozdniakov

CONFERENCE ON THE USE OF RADIOACTIVE ISOTOPES IN ANALYTICAL CHEMISTRY

An All-Union Conference organized by the Chemical Sciences Section of the USSR Academy of Sciences and the Commission on Analytical Chemistry of the V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, was held in Moscow on December 2-4, 1957; the Conference was devoted to questions connected with the use of radioactive isotopes in analytical chemistry.

More than 450 scientific workers and representatives of production organizations participated. In addition to Soviet research workers, many foreign scientists from several countries took part (England, Bulgaria, Hungary, China, Poland, Rumania, USA, Czechoslovakia, and Yugoslavia).

Fifty reports were read at the Conference, 26 of these being the subjects of discussion at the Conference.

The plenary session was opened by Academician A.P. Vinogradov who outlined the basic uses of radioactive isotopes in analytical chemistry. Academician A.P. Vinogradov emphasized that at the present moment the radioactive isotopes of most of the elements of the periodic system are in use in analytical practice, and that their use is becoming as commonplace as the classical methods of qualitative and quantitative analysis.

At the plenary session, the report of A.V. Nikolaev, A.A. Sorokina and A.S. Maslennikov on the use of radioactive isotopes for developing methods for the separation of the rare earths was read. In their report, L.P. Alimarin and G.N. Bilimovich gave results on the use of isotope dilution for the determination of certain rare elements. Using the radioisotopes Nb^{95}, Zr^{95} and Ta^{182} the authors have developed methods for separating tantalum from titanium, zirconium and niobium, and for determination of tantalum by the isotope dilution method. The methods have been checked on the analysis of rocks and alloys.

The report given by A.N. Ermakov, V.K. Beliaeva and I.N. Marov was devoted to the use of labelled atoms (Zr^{95} and Hf^{181}) for the study of complex formation of zirconium and hafnium with the oxalate ion by an anion-exchange method. Taking this as an example, and using anion-exchange resins, the possibility was demonstrated of calculating the stability constants of the complex compounds of multi-charged ions which form stable complexes in strongly acid media with weakly dissociating materials.

I.M. Korenman and F.R. Sheianova reported on the use of nonisotopic indicators for solving a number of analytical problems, and adduced a large amount of experimental data on radiometric titration. The authors also demonstrated the possibility of determining solubility by using nonisotopic indicators (tetrathiocyanomercuriates, nitrocobaltiates, etc.).

At one of the sectional sessions A.I. Kulak gave a report on the quantitative determination of microamounts of certain metals present as impurities in ferric oxide by a radioactivation method.

The report of V.B. Gaidadymov and L.I. Il'ina on the analysis of binary tantalum-niobium alloys by means of reflection (back-scattering) of β-rays, attracted special attention. This method permits analysis of samples in different physical forms: powders, moldings and plates; the experimental error does not exceed 0.5% absolute for tantalum contents ranging from 2 to 98%. An analysis takes three to five minutes.

The subject of G.S. Rozhavskii and I.E. Zimakov's report was multi-radioactive dilution for the determination of small amounts of impurities.

M.B. Neiman, V.E. Efremov and V.N. Panfilov reported on determination of alcohols by the isotope dilution method.

K.B. Iatsimirskii and E.N. Rosliakova discussed radiometric titration and the use of solutions of complex compounds of cobalt 60.

I.P. Alimarin, A.K. Babko, V.I. Kuznetsov, N.P. Komar', K.B. Iatsimirskii and others took an active part in the discussion of the reports.

Professor I.M. Kolthoff (USA) gave a report with a wealth of detail on the use of radioactive isotopes for the study of aging of crystalline precipitates.

A.K. Lavrukhina discussed some characteristics of the technique of radiochemical analysis. Isolation of some short-lived isotopes from complex mixtures was discussed in the report of V.P. Shvedov and L.I. Ivanova, while M.M. Senlavin reported on the use of radioactive isotopes in chromatography. On the basis of experimental work on the adsorption of ruthenium from solution onto ion-exchange resins (E.I. Il'enko, B.P. Nikol'skii and A.M. Trofimov), the authors suggested an original method for the quantitative extraction of ruthenium from solution. Other reports were heard with equal interest: a carbonate method for removing micro-amounts of uranium from weighable amounts of iron (I.E. Starik, F.E. Starik and A.N. Apollonova); a study of precipitation conditions in ternary systems: dye-base, metal, halogen (A.K. Babko and P.V. Marchenko); isolation of uranium from sea water by means of organic coprecipitants (V.I. Kuznetsov and T.G. Akimova); coprecipitation of certain elements at low concentrations of the latter with metal hydroxides (Iu.V. Morachevskii and A.I. Novikov).

At the last session G.I. Irving (England) reported on the analytical chemistry of indium. A report on the study of the analytical chemistry of francium by means of the radioactive isotope Fr^{212} was then read (A.K. Lavrukhina, S.S. Rodin). The report led to a lively discussion. In particular, K.B. Iatsimirskii pointed out the general rules relating the solubility of the alkali metals to the dimensions of the cation and the anion; N.B. Mikheev spoke on the isomorphism of the salts of cesium and francium with silicotungstic and phosphotungstic acids; V.I. Kuznetsov communicated some ideas on organic coprecipitants for francium; I.V. Tananaev suggested the use of a series of mixed ferrocyanides for coprecipitation of francium.

The following reports were also heard: the use of radioactive indicators for checking on methods of isolating niobium (Iu.I. Bykovskaia); a technique for using radioactive indicators for controlling the production of rare metals (A.A. Gridik and N.I. Marunina); the use of Ca^{45} for determination of nonmetallic inclusions in steel (M.I. Tsekhanskii, N.I. Shishkina, K.V. Khusnolarov and G.D. Susloparov); the use of Cl^{36} for the quantitative determination of hexachlorocyclohexane isomers in technical hexachlorane (P.V. Zimakov and L.A. Krasnousov); the use of labelled atoms for determination of the efficiency of fractionation of gaseous hydrocarbons (K.I. Karasev).

In his concluding remarks A.P. Vinogradov noted that analytical chemistry is, at present, a very important user of radioactive isotopes for the solution of many chemical questions. It is hoped, in the not too distant future, to discuss questions related to the apparatus and to the dosimetry of various types of radiation which are applicable to analytical chemical problems.

A.N. Ermakov

CRITICISM AND BIBLIOGRAPHY

"The Bases of Qualitative Chemical Analysis," N.L. Komar'. The A.M. Gor'ky Kharkov State University Press, 1955. Printing 10,000. Price 10 rubles 50 kopecks.

The book under review is a theoretical introduction to a course of qualitative chemical analysis.

The book consists of 19 chapters in which are set forth:

1. A brief account of the history of analytical chemistry in Russia;

2. Necessary information on the theory of solution and precipitation of sparingly soluble materials;

3. The application of the law of mass action to ionic equilibria;

4. The theory and practice of the application of organic reagents in chemical analysis;

5. The sensitivity of chemical reactions.

The book contains about 100 systematically chosen examples illustrating the application of the theory of ionic equilibrium in chemical analysis. The appendix contains tables of constants for calculating equilibrium during precipitation, complex-formation, oxidation, reduction, and other chemical reactions.

The book is the result of the penetrating, creative, and scientific research work of the author in the theory of analytical chemistry.

All the questions discussed are set forth at a high theoretical level and are successfully illustrated by numerical problems which certainly help in assimilating the material set forth.

Deserving of particular attention are Chapters XI, XIII and XV devoted to precipitation of sparingly soluble materials under conditions of supersaturation and heterogeneous equilibrium. By making use of a number of actual examples, the author has shown with perfect clearness and mathematical accuracy that the well-known equation of so-called relative supersaturation is of very limited application. The thermodynamic equation of V. Thomson which takes into account many individual properties of sparingly soluble materials (surface tension, molecular weight, density, crystal radius) permits a more accurate characterization of precipitation from homogeneous solutions.

A superficial acquaintance with the book gives the impression that it is overloaded with calculating material. But a more thorough study of the book dispels this impression: the successfully chosen and, from a mathematical point of view, reproachless examples from various branches of chemical analysis disclose the essence of the chemical processes which occur in aqueous solutions, and allow one to make a conscious choice of the conditions to be used in chemical experiments.

All the same, some of the chapters in the book under review do not contain an exhaustive exposition of the material. This is true of Chapter VI "Indicator Theory," and Chapter XIV, in the section on coprecipitation.

Bearing in mind that the book is designed for students in the second course in chemical faculties in state universities, during a study of qualitative analysis, a full discussion of these questions should be related to the course of quantitative analysis.

The scientific-theoretical level of the book leads one to express the opinion that it would be more suitably called "The Theoretical Bases of Chemical Analysis."

This book is a very valuable original textbook on the theory of analytical chemistry, important to both Russian

and foreign literature, and will undoubtedly play a very essential part in preparing specialists in chemistry in state universities; it should become a bench book for research chemists.

A. Tikhonov

THE ORGANIZING COMMITTEE OF THE EIGHTH MENDELEEV CONFERENCE ON GENERAL AND APPLIED CHEMISTRY

INFORMATION

The Organizing Committee of the Eighth Mendeleev Conference wishes to inform all chemists in the Soviet Union that on the 8-13th of December, 1958, there will be held in Moscow the Eighth Mendeleev Conference on General and Applied Chemistry.

In addition to plenary sessions at which communications will be read on the basic problems of modern chemistry, reports will also be heard and discussed on the following sections: 1) inorganic chemistry and technology (including rare elements); 2) organic chemistry and technology; 3) analytical chemistry; 4) physical chemistry; 5) colloid chemistry; 6) chemistry and technology of polymers; 7) chemistry of natural compounds and biochemistry; 8) agronomic chemistry; 9) chemistry and chemical technology of fuel; 10) chemistry and technology of food-stuffs; 11) chemistry and technology of silicates; 12) radiochemistry and the chemistry of isotopes; 13) theoretical and applied electrochemistry; 14) chemistry of metals and alloys; 15) the economics, planning, and organization of chemical production; 16) basic processes and apparatus of chemical technology; and 17) the history of chemistry and chemical technology.

In addition, a symposium will be held on advanced chemical education. The participants at the session will be delegates chosen by the individual branches of the D.I. Mendeleev All-Union Chemical Society, and those given a personal invitation by the Organizing Committee.

Others may take part in the conference, including young specialists and students by Guest Tickets.

Payment for personal expenses incurred by those coming from outside Moscow should be made by the institution or enterprise at which the given person works, or should be set down to the D.I. Mendeleev All-Union Chemical Society.

Participants may read one report.

The reports to be given at the session may be of two kinds:

a) reports containing new unpublished studies of a theoretical or experimental nature. In contrast to scientific communications read at conferences devoted to special topics, the reports to be read at the projected session should be of a more general character for science and practice. Not more than 15 minutes will be devoted to such reports;

b) brief communications – predominantly for young chemists – devoted to only new facts, new observations or theoretical ideas; five minutes will be devoted to this category.

Those wishing to read reports or brief communications at the session should inform the Organizing Committee of their intention and should send a signed report and forms not later than April 15, 1958 (Moscow, V-49, P/Ia 3085).

The report should only be printed on one side of the paper; two copies should be sent and the text should not occupy more than three typewritten pages – double spacing – including tables or drawings. Texts requiring complicated type setting should be avoided.

The report should be recommended by a scientific or educational establishment, an industrial enterprise, or by a branch of the All-Union Chemical Society. The report should be sent to the Organizing Committee un-

der the signature of the head of the institution or establishment concerned. Reports accepted by the Committee will be published prior to the session.

Inquiries of a general nature should be sent to the following address: Moscow V-71, Leninskii Prospect, Chemical Sciences Section of the USSR Academy of Sciences, Chief Scientific Secretary of the Organizing Committee of the Mendeleev Conference, Professor V.V. Kozlov.

Organizing Committee of the Eighth
Mendeleev Conference

USSR ACADEMY OF SCIENCES

CHEMICAL SCIENCES SECTION

COMPETITIONS FOR PRIZES OF THE USSR ACADEMY OF SCIENCES

The Chemical Sciences Section of the USSR Academy of Sciences wishes to announce that during 1958 competitions will be held for the following prizes of the USSR Academy of Sciences:

1. The A.M. Butlerov Prize of 20,000 rubles for work in organic chemistry.

2. The N.S. Kurnakov Prize of 10,000 rubles for outstanding work in the field of general chemistry, and physicochemical analysis and its applications.

Work to be considered for these prizes can be presented by scientific societies, scientific-research institutes, higher educational institutions, departments, social organizations, and private citizens of the USSR.

Only published work can be considered for these prizes.

The work should be sent to the Chemical Sciences Section of the USSR Academy of Sciences (Moscow, V-71, Leninskii Prospect, 14) and should be marked "For the Competition for the A.M. Butlerov (N.S. Kurnakov) Prize"; three copies should be sent. A short biographical note on the candidate for the prize and a list of his major work and inventions should also be sent. Papers should be submitted by June 1, 1958.

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9. Physicochemical Properties of Ion Exchange Resins.
10. Properties of some Cation Exchange Resins and the Possibility of Using Them in the Medical and Food Industries.
11. Properties of Certain Anion Exchange Resins and the Possibility of Using Them in the Medical and Food Industries.
12. Purification of Certain Chemical Compounds by Means of Ion Exchange Sorbents.
13. Possibility of Using Ion Exchange Resins for Obtaining Drinking Water of High Mineral Content.
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